N. Sevryukov

NONFERROUS METALLURGY

Mir Publishers

Moscow

N. Sevryukov, D.Sc. (Tech.), taught a course in metallurgy at the Moscow Institute of Nonferrous Metals and Gold for 15 years. Now he is Professor of the Patrice Lumumba Peoples' Friendship University.

Written before by N. Sevryukov with the participation of B. Kuz'-min and E. Tchelishchev was book *General Metallurgy* which covered ferrous and nonferrous metals. It was published in the USSR in Russian (1954 and 1962) in English (1965 and 1969) and in Arabian (1971). More than that, *General Metallurgy* has been translated in China (1957-1959), Korea (1959), Rumanie (1957), Czechoslovakia (1958) and partially in Bulgaria (1960).

In addition N. Sevryukov co-authored *Tin Metallurgy* (1964) and *Nonferrous Metallurgy* (1957).

The author is in a position to bring together all of the new and interesting factors and developments in the field of nonferrous metallurgy. His experience and contact with designers and users of metallurgical equipment have given him a broad yet thorough grasp of the problems and the steps toward their solutions in the neverending search for better utilization of the capabilities of both man and machine.

NONFERROUS METALLURGY presents a moderate practical application with major emphasis on the theoretical treatment of the topic. It is a textbook for secondary technical schools and colleges. The book outlines the techniques for ore dressing and gives an adequate survey of nonferrous metals recovery and utilization of by-products.

The areas of metallurgical fuels and refractory materials are thoroughly covered as well.

The first chapters of the book are an advanced introduction and guide to principles of metallurgy. The techniques discussed include metallurgy of copper, nickel, lead, zinc, aluminium, magnesium, titanium, tungsten and molybdenum.

In conclusion it may be said that this work is a basic treatise and reference book for anyone interested in nonferrous metallurgy.

About the Publishers

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Н. СЕВРЮКОВ

Металлургия цветных металлов

ИЗДАТЕЛЬСТВО «МЕТАЛЛУРГИЯ»
МОСКВА

N. Sevryukov

NONFERROUS METALLURGY

Translated
from
the
Russian
by
I. SAVIN

Mir
Publishers
Moscow

First published 1975

The Russian Alphabet and Transliteration

А а	a	К к	k	Х х	kh
Б б	b	Л л	l	Ц ц	ts
В в	v	М м	m	Ч ч	ch
Г г	g	Н н	n	Ш ш	sh
Д д	d	О о	o	Щ щ	shch
Е е	e	П п	p	ъ	″
Ё ё	ë	Р р	r	ы	y
Ж ж	zh	С с	s	ь	′
З з	z	Т т	t	Э э	e
И и	i	У у	u	Ю ю	yu
Й й	y	Ф ф	f	Я я	ya

The Greek Alphabet

Α α	Alpha	Ι ι	Iota	Ρ ρ	Rho
Β β	Beta	Κ κ	Kappa	Σ σ	Sigma
Γ γ	Gamma	Λ λ	Lambda	Τ τ	Tau
Δ δ	Delta	Μ μ	Mu	Υ υ	Upsilon
Ε ε	Epsilon	Ν ν	Nu	Φ φ	Phi
Ζ ξ	Zeta	Ξ ξ	Xi	Χ χ	Chi
Η η	Eta	Ο ο	Omicron	Ψ ψ	Psi
Θ θ	Theta	Π π	Pi	Ω ω	Omega

На английском языке

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INTRODUCTION

Since the time when metals replaced wood and stone in the everyday life of our ancestors, the demand for metals is in a continual rise. They became irreplaceable materials in many branches of industry and engineering, such as machine and engine building, construction and transport, electrical engineering and electronics. Production and consumption of metals rise steadily from year to year.

The ancient art of extracting metals, which in the Middle Ages was more often than not a family or a shop secret, evolved, with the development of chemistry and engineering, into a metals manufacturing science, the metallurgy.

Metallurgy is concerned with the chemical principles underlying the winning of metals from ores and the necessary physical and chemical conditions. In other words, it represents the chemical process techniques for manufacturing metals.

The founding of metallurgy as a science is rightly accredited to M. V. Lomonosov whose book "The Initial Bases of Metallurgy or Smelting" (1763) was the cornerstone of scientific metals' manufacture.

Singling metallurgy out of other companion manufactures, M. V. Lomonosov wrote: "The field of metallurgy ends there and then where it supplies pure metals and semi-metals to useful applications".*

Much the same in our times, when the metallurgy begins with the delivery of ore or other raw materials to a metallurgical plant and ends in the manufacture of pure metal or a standard alloy suitable for use in other industries. Inclusion of rolling, forging, stamping or any other mecha-

* At that time, the semi-metals were bismuth and antimony.

nical or heat treatment of metals should be considered irregular and contrary to logic.

Prior to the metallurgical processes ores are crushed, ground and enriched (concentrated) by removing gangue.

Winning of metals may be rendered simpler or more complicated by ore enrichment performance. Some ore dressing methods are used in parallel with purely metallurgical processing stages. Therefore, a metallurgist should be conversant with the enrichment principles and this is why the methods are often discussed in textbooks on metallurgy although ore dressing is a realm quite different from the metallurgy.

Metallurgy was developed on the basis of advances in chemistry, which is considered to have begun in the forties of the 18th century, when M. V. Lomonosov expounded his molecular-atomistic views in the initially formulated law of the conservation of mass*.

At the end of the 18th century Lavoisier had shown that metals, complex substances according to the then current ideas, were actually simple bodies, whereas oxides, by contrast, were complex substances. Soon after, Proust established the second basic law of chemistry or the law of constant proportions.

What contributed to a particularly rapid development of chemistry, and of metallurgy as well, was the discovery by D. I. Mendeleev of the periodic law (1869).

At the beginning of the 19th century chemists knew 30 chemical elements only and metallurgists knew how to manufacture 10 of these for centuries known metals. The periodic law facilitated the search for and the study of new elements, and towards the beginning of this century the known elements totaled 61.

This period was also the beginning of a fast development of railway transport, automotive and aviation industries

* In the international system, the unit of mass is kilogram (kg). Whenever a quantity of a substance is considered, e.g., the consumption of a metal or a material for the manufacture of some items, the word mass should be spoken of. Therefore, the terms "mass composition", "mass consumption", "mass heat capacity", "mass fraction", "per cent by mass" should be used in preference to the terms "weight composition", "weight consumption", "weight heat capacity", "weight fraction" and "per cent by weight".

as well as of complex military equipment. New industries called for new materials with various properties, including alloys containing aluminium, magnesium, zinc, nickel and many other elements.

In the last century metallurgists relied chiefly on manual labour which was very laborious and unsafe in many cases. The engineering techniques of the 20th century radically transformed industrial production, and today metallurgical plants are large mechanized and even partly automated enterprises.

Today, the metallurgy is a vast branch of industry, which processes great amounts of raw materials and consumes

Table 1

Yearly Output of Metals in Mid 50-ies of 20th Century

World output, t/year	Metal	World output, t/year	Metal
$(5\text{-}6)\cdot10^8$	Iron	$(1\text{-}10)\cdot10^3$	Silver, Mercury, Gold, Bismuth, Beryllium
$1\cdot10^7$	Aluminium, Copper	$(1\text{-}10)\cdot10^2$	Tantalum, Zirconium
$(4\text{-}5)\cdot10^6$	Zinc, Lead		
$(3\text{-}6)\cdot10^5$	Nickel, Tin, Magnesium	$(1\text{-}10)\cdot10$	Gallium, Rhenium, Platinum, Palladium, Indium
$(1\text{-}4)\cdot10^4$	Antimony, Tungsten, Cobalt, Cadmium, Lithium, Molybdenum, Uranium, Vanadium, Niobium, Titanium	$(1\text{-}10)\cdot10^{-1}$	Iridium, Rhodium

much fuel and energy. Therefore, it cannot be thought of separately from an adequately developed electric power base and powerful means of transport. An idea of present-day output of metals is given in Table 1.

A small yield of product is not yet evidence of a small production scale. Many ores are very lean, and the manufacture of, say, 1 ton of copper requires the treatment of more than 100 tons of ore (for ore containing 1% of copper).

The cost of a metal is governed by expenses for its manufacture, and it is the higher, the leaner the ore and the more complicated its treatment.

Modern engineering, and, particularly, nuclear power generation and electronics, call for metals of high purity which contain not more than thousandths and sometimes millionths of 1% of impurities. Attainment of this purity is rendered even more complicated by the necessity of careful consumption of mineral resources and of a most complete recovery of metals the latter carry, i.e., of a complete recovery of all values.

Another problem in present-day metallurgy is the requirement to decontaminate all wastes so as to avoid polluting the atmosphere, water reservoirs and the surroundings. This new major requirement will—and there is no doubt about it—bring about substantial changes in the traditional methods of many a metallurgical technique.

METALLURGY FUNDAMENTALS

1. Metals and Their Classification

Metals consist of geometrically regular crystals that form a characteristic pattern, or lattice, whose sites are occupied by continuously vibrating ions and atoms. Electrons of outermost shells are but weakly bonded to the nucleus, tend to break away and return, the atoms thus being converted to ions, and the ions, to atoms.

A crystalline lattice of a metal can be thought of as composed of atoms and ions, permeated by freely and irregularly moving electrons. Fig. 1 illustrates the most frequent types of lattices.

Lattice sites should be considered centres of compactly packed spherical atoms and ions that occupy about 70% of the space. Vibration amplitudes depend on the temperature and increase with it. At the melting point they are so great that the lattice falls apart, the atoms and the ions loosing their permanent sites and moving about at random which is characteristic of a liquid state. The bonds between ions and electrons are metallic, and between the atoms, covalent. The ratio of these kinds of chemical bonds affects the number of freely moving electrons, whose quantity is the greater, the more apparent are the metallic properties of the element.

The strength and elasticity of metallic bonding and a dense packing of crystalline lattices explain many physical and mechanical properties of metals.

External mechanical action may shift crystalline lattice, but the bonds between the ions and the electrons are not disturbed because of their free mobility. This also underlies the strength and the plasticity of metals, which thus can change shape without loosing the internal bonding among particles.

The free motion of electrons in the spaces between lattice sites explains the high electric conductivity of metals when a potential is applied to them, zigzag motion of the electrons

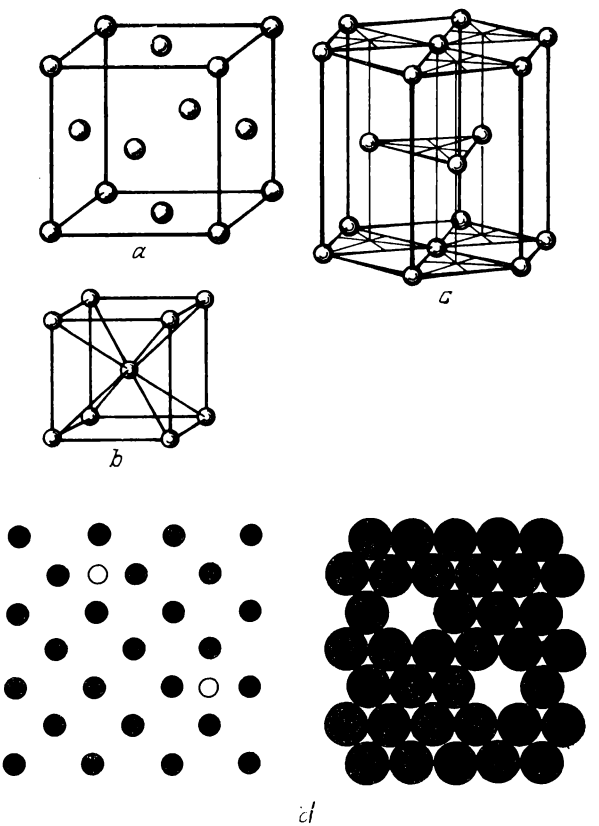

Fig. 1. Simplest crystal lattice structures of metals
a —copper (similar to Au, Ag, Al, Pt); *b*—iron (similar to K, Ba); c—magnesium; *d*—vacancies

then being transformed into an oriented flow. The ion and atom vibration amplitudes increase with the temperature, while the rapidly growing number of collisions intensively scatter electrons, with the effect that the electric conducti-

vity falls down. The same phenomenon is observed in the presence of impurities. At temperatures close to absolute zero, vibration in the lattice sites almost ceases, and the electrical conductivity of some metals sharply rises whereby the electrical resistivity of certain metals essentially vanishes at temperatures close to absolute zero (0°K). This effect known as superconductivity opens new vistas in science and engineering.

Heat conductivity of metals is an effect of electron motion as well as ion and atom vibrations. This explains why electrical and thermal conductivities are properties varying in parallel. Metals of a high electrical conductivity are also highly heat conductive.

When heated, metals may emit free electrons. This phenomenon, thermionic emission, is governed by temperature and by lattice structure. In some metals its value is particularly great, this being put to a useful application in electronics.

Liquid metals differ from solid ones by relatively weaker bonds among atoms and ions, but electrons are still free to move, and the liquid metals are as electrically and thermally conductive as metals in solid form.

Some metals have different types of lattice at various temperatures. The change from one type lattice to another affects the spacing and the mutual arrangement of sites and has a material effect on the properties of the polymorphic modifications. For example, tin, known at common temperatures as a plastic lustrous metal with a density of 7.29 g/cm^3 (β-tin) turns to a grayish powder of density 5.85 g/cm^3 (α-tin) at temperatures below 13.2°C, this change being particularly rapid in case of a supercooling. Similar transformations are characteristic of many other elements. Some metals are mutually soluble in liquid or solid states, some form intermetallic chemical compounds. All this forms new crystalline systems with widely varying characteristics, i.e., alloys, thus offering many possibilities for creating materials of desired properties. Thousands of binary, ternary and more complicated metallic alloys are used in modern engineering.

Alloys are manufactured not only by mixing liquid metals, but by sintering powders or dissolving an element in the superficial layer of a solid metal.

Ability to undergo elastic and plastic deformation, high electrical and thermal conductivities and other particularities make up a complex of characteristic properties of metals which are lacking in other solid bodies, i.e., wood, stone, plastics. This explains the indisputable recognition of metals and alloys as the major materials of modern engineering.

It should be noted that all valuable properties of metals and alloys are affected by their purity and mechanical

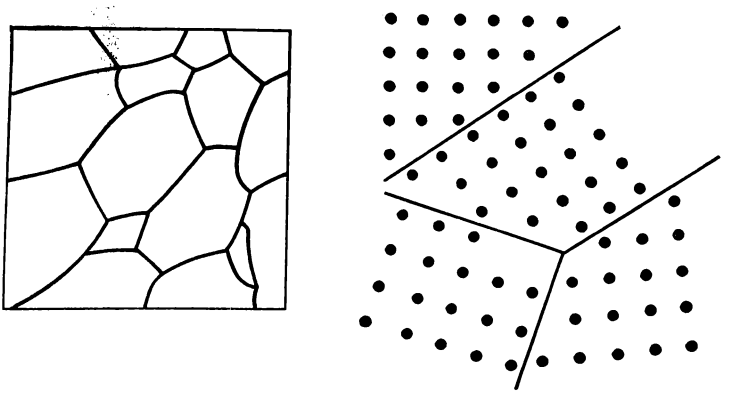

Fig. 2. Grains oriented at different angles

working. Since it would be beyond the scope of the present book to delve into the field of physical metallurgy and the physics of metals, let us note but the crucial points. When a metal or alloy solidifies resultant crystals assemble into grains (Fig. 2). Inside of each grain, the crystals are similarly oriented whereas in adjacent grains they are differently oriented. Impurities and gas inclusions often tend to accumulate at the boundaries between grains, thus affecting adversely, among other things, the strength. Grains may also carry structural defects, which weaken them, i.e., the point defects, when crystal lattice sites are not filled by structural components, in other words, the crystals have vacancies, which may sometimes be occupied by impurities (Fig. 1*d*). The impurities often tend to wedge themselves between lattice sites. One-dimensional imperfections or

dislocations result from the shift of crystal layers (in a manner similar to that of playing cards in a pack), and they may be of the edge (linear) and screw types.

Such imperfections take origin in the solidification of a molten metal (alloy) or its deformation by forging, stamping, and rolling. Their number may be as high as 10^6 to 10^8 per cubic centimetre.

Incidence of oxygen and nitrogen impurities (which produce oxide or nitride micro-inclusions, insoluble in the metal) and other solid constituents prevent shifts in the direction of dislocations and make a metal, otherwise of ready forgeability, hard and brittle. This was the case with titanium, which was considered brittle for a long period of time, but proved itself to be ductile when obtained in a pure state.

Thus, the mechanical properties of metals are often but loosely related to the structure of atoms and crystals, being governed to a greater degree by purity and mechanical working they undergo.

As known from a course in chemistry, metals are elements whose oxides combine with water to give bases, in contrast to metalloid oxides that yield acids. Hydroxides of many elements, commonly classed with metals, as, zinc, aluminium and tin, are amphoteric, i.e., they exhibit both basic and acid properties. Thus, there is no clear-cut differentiation of metals and metalloids, each of these chemical elements possessing, but to a different degree, properties characteristic of either.

However, a conventional boundary can be drawn between metals and metalloids by assuming the chief particularity of metals to be the presence in the crystalline lattice of roaming electrons. In D. I. Mendeleev's periodic table of the elements given in Table 2, the structure of atoms is complemented by the types of crystalline lattices of metals and data on density and specific electrical resistance at an ordinary temperature. The specific electric resistance is directly related to the number of free electrons and may serve as a most illustrative measure of metallic properties.

Manganese, although amphoteric, exhibits to a large degree the properties of a metal. Carbon, by contrast, is a typical metalloid. The former has a distorted cubic lattice

and a specific electrical resistivity of 185 μohm-cm. The latter's resistivity is 1375.0 μohm-cm, min., only when it crystallizes in a hexagon-latticed graphite, whereas the resistivity of its cubic modification (diamond) is more than $5 \cdot 10^4$ ohm-cm. Having assumed resistivity values as a basis of differentiation, we have not shaded metals, 81 in all, in Table 2. Next, if the field of metallurgy is limited to elements composing the earth's crust, it is necessary to eliminate Fr, Tc, Pm and the actinides, beginning with Am, and so restrict the scope of metallurgy to the manufacture of 68 elements.

Still one more conventionality stems from, first, the current requirements of a complex processing of ores, which is aimed at recovering all its values, and involves an extensive production of alloys, and, second, from the traditionally established practice. This conventionality is that many non-metals, i.e., silicon, germanium, sulphur, selenium, tellurium and other metalloids that are commonly, but erroneously, classed with metals, are often manufactured at metallurgical plants.

In the periodic table of elements of D.I. Mendeleev, metals are found in all the groups, except for the zero, sixth and the seventh ones. In each of the main sub-groups, metallic properties grow in intensity from the top to the bottom, and weaken from left to right in each of the seven horizontal rows. All these variations result from electron structures of atoms.

The chemical activity of metals may be described by their oxidation-reduction potentials as is given in Table 3.

It should be remembered that the equilibrium oxidation-reduction potential* between a metal and a molar solution of its ions (more specifically, a solution of an activity of 1 gram-ion in 1000 g of water) describes the capacity of an atom to give off its electrons, or to oxidize. The greater the algebraic value of the potential, the lesser the reducing ability and the chemical activity of a metal.

Metals of a negative potential are readily oxidizable, some of them even by water, and therefore, they occur naturally as chemical compounds only, i.e., oxides, halides,

* Often termed the electrode or the electrochemical potential.

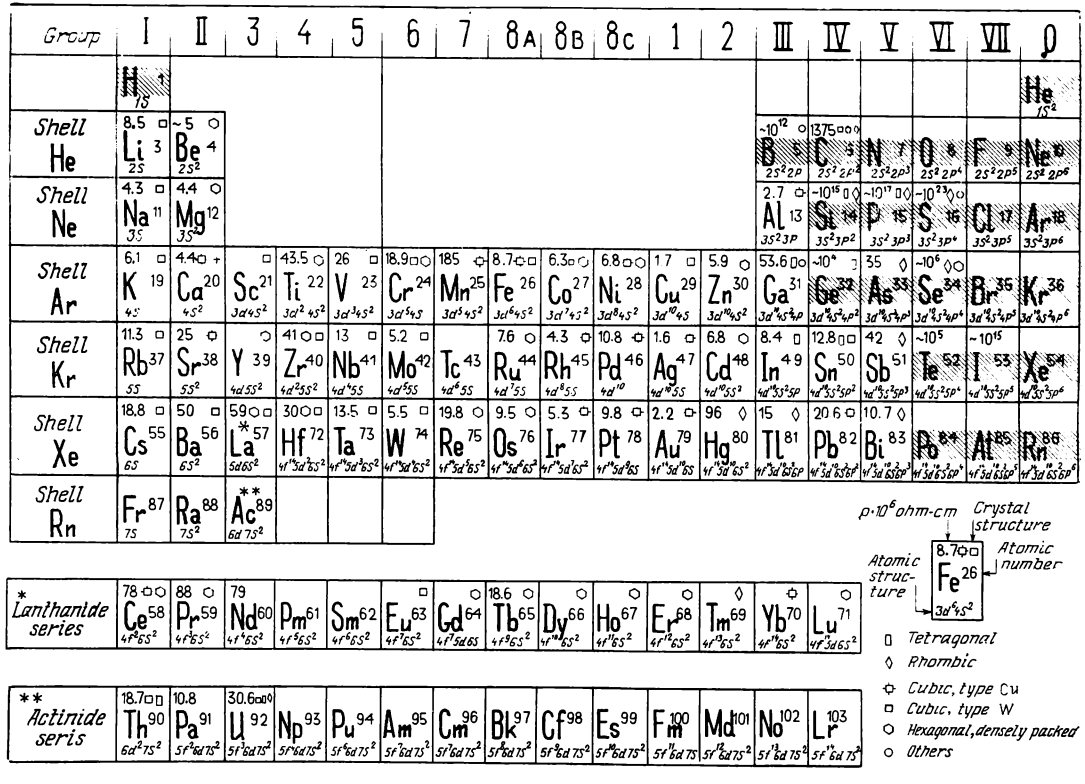
Group
I
II
3
4
5
6
7
8A
8B
8c
1
2
III
IV
V
VI
VIII
0
Shell He
Shell Ne
Shell Ar
Shell Kr
Shell Xe
Shell Rn
H 1 1S
He 2 1S²
Li 3 2S
Be 4 2S²
B 5 2S² 2P
C 6 2S² 2P²
N 7 2S² 2P³
O 8 2S² 2P⁴
F 9 2S² 2P⁵
Ne 10 2S² 2P⁶
Na 11 3S
Mg 12 3S²
Al 13 3S² 3P
Si 14 3S² 3P²
P 15 3S² 3P³
S 16 3S² 3P⁴
Cl 17 3S² 3P⁵
Ar 18 3S² 3P⁶
K 19 4S
Ca 20 4S²
Sc 21 3d 4S²
Ti 22 3d² 4S²
V 23 3d³ 4S²
Cr 24 3d⁵ 4S
Mn 25 3d⁵ 4S²
Fe 26 3d⁶ 4S²
Co 27 3d⁷ 4S²
Ni 28 3d⁸ 4S²
Cu 29 3d¹⁰ 4S
Zn 30 3d¹⁰ 4S²
Ga 31 3d¹⁰ 4S² 4P
Ge 32 3d¹⁰ 4S² 4P²
As 33 3d¹⁰ 4S² 4P³
Se 34 3d¹⁰ 4S² 4P⁴
Br 35 3d¹⁰ 4S² 4P⁵
Kr 36 3d¹⁰ 4S² 4P⁶
Rb 37 5S
Sr 38 5S²
Y 39 4d 5S²
Zr 40 4d² 5S²
Nb 41 4d⁴ 5S
Mo 42 4d⁵ 5S
Tc 43 4d⁶ 5S
Ru 44 4d⁷ 5S
Rh 45 4d⁸ 5S
Pd 46 4d¹⁰
Ag 47 4d¹⁰ 5S
Cd 48 4d¹⁰ 5S²
In 49 4d¹⁰ 5S² 5P
Sn 50 4d¹⁰ 5S² 5P²
Sb 51 4d¹⁰ 5S² 5P³
Te 52 4d¹⁰ 5S² 5P⁴
I 53 4d¹⁰ 5S² 5P⁵
Xe 54 4d¹⁰ 5S² 5P⁶
Cs 55 6S
Ba 56 6S²
La 57 5d 6S²
Hf 72 4f¹⁴ 5d² 6S²
Ta 73 4f¹⁴ 5d³ 6S²
W 74 4f¹⁴ 5d⁴ 6S²
Re 75 4f¹⁴ 5d⁵ 6S²
Os 76 4f¹⁴ 5d⁶ 6S²
Ir 77 4f¹⁴ 5d⁷ 6S²
Pt 78 4f¹⁴ 5d⁹ 6S
Au 79 4f¹⁴ 5d¹⁰ 6S
Hg 80 4f¹⁴ 5d¹⁰ 6S²
Tl 81 4f¹⁴ 5d¹⁰ 6S² 6P
Pb 82 4f¹⁴ 5d¹⁰ 6S² 6P²
Bi 83 4f¹⁴ 5d¹⁰ 6S² 6P³
Po 84 4f¹⁴ 5d¹⁰ 6S² 6P⁴
At 85 4f¹⁴ 5d¹⁰ 6S² 6P⁵
Rn 86 4f¹⁴ 5d¹⁰ 6S² 6P⁶
Fr 87 7S
Ra 88 7S²
Ac 89 6d 7S²
* Lanthanide series
Ce 58 4f¹ 6S² 5d
Pr 59 4f³ 6S²
Nd 60 4f⁴ 6S²
Pm 61 4f⁵ 6S²
Sm 62 4f⁶ 6S²
Eu 63 4f⁷ 6S²
Gd 64 4f⁷ 5d 6S
Tb 65 4f⁹ 6S²
Dy 66 4f¹⁰ 6S²
Ho 67 4f¹¹ 6S²
Er 68 4f¹² 6S²
Tm 69 4f¹³ 6S²
Yb 70 4f¹⁴ 6S²
Lu 71 4f¹⁴ 5d 6S²
** Actinide series
Th 90 6d² 7S²
Pa 91 5f² 6d 7S²
U 92 5f³ 6d 7S²
Np 93 5f⁴ 6d 7S²
Pu 94 5f⁶ 7S²
Am 95 5f⁷ 7S²
Cm 96 5f⁷ 6d 7S²
Bk 97 5f⁸ 6d 7S²
Cf 98 5f¹⁰ 7S²
Es 99 5f¹¹ 6d 7S²
Fm 100 5f¹² 6d 7S²
Md 101 5f¹³ 6d 7S²
No 102 5f¹⁴ 7S²
Lr 103 5f¹⁴ 6d 7S²
ρ·10⁶ ohm-cm
Crystal structure
Atomic structure
Atomic number
8.7 Fe 26 3d⁶ 4S²
Tetragonal
Rhombic
Cubic, type Cu
Cubic, type W
Hexagonal, densely packed
Others

Table 3

Oxidation-Reduction Potentials According to Hydrogen Scale at 20 °C and Some Properties of Metals

$H_2 - 2\bar{e} \rightleftarrows 2H^+$; $E^\circ = 0.00$

Metal	Oxidation-reduction system	Normal potential, V	Oxidation in the air	Displacement of hydrogen from acids	Temperature of reduction of oxides by carbon, °C	Natural occurrence
1. Calcium	$Ca - 2\bar{e} \rightleftarrows Ca^{2+}$	−2.87	Rapid	Violent	Above 1000°	Halides and oxide compounds
2. Sodium	$Na - \bar{e} \rightleftarrows Na^+$	−2.71				
3. Magnesium	$Mg - 2\bar{e} \rightleftarrows Mg^{2+}$	−2.37	Slow, at various rates	Slow, at various rates		Oxide compounds *
4. Aluminium	$Al - 3\bar{e} \rightleftarrows Al^{3+}$	−1.66				
5. Titanium	$Ti - 2\bar{e} \rightleftarrows Ti^{2+}$	−1.63				
6. Zinc	$Zn - 2\bar{e} \rightleftarrows Zn^{2+}$	−0.76			Below 1000°	Sulphides and oxide compounds
7. Iron	$Fe - 2\bar{e} \rightleftarrows Fe^{2+}$	−0.44				
8. Cadmium	$Cd - 2\bar{e} \rightleftarrows Cd^{2+}$	−0.40				
9. Cobalt	$Co - 2\bar{e} \rightleftarrows Co^{2+}$	−0.28				
10. Nickel	$Ni - 2\bar{e} \rightleftarrows Ni^{2+}$	−0.25				
11. Tin	$Sn - 2\bar{e} \rightleftarrows Sn^{2+}$	−0.14				
12. Lead	$Pb - 2\bar{e} \rightleftarrows Pb^{2+}$	−0.13				
13. Copper	$Cu - 2\bar{e} \rightleftarrows Cu^{2+}$	+0.34	Not oxidized	Fail to displace	Oxides are unstable in air	Sulphides and element state **
14. Mercury	$Hg - 2\bar{e} \rightleftarrows Hg^{2+}$	+0.79				
15. Silver	$Ag - \bar{e} \rightleftarrows Ag^+$	+0.80				
16. Gold	$Au - \bar{e} \rightleftarrows Au^+$	+1.50				

* Carbonates, silicates and salts of other oxygen-bearing acids.
** Silver also in the form of cerargyrite (AgCl).

Table 4

Industrial Classification of Metals

Group	Subgroup	Metals
errous etals		Fe Iron and its alloys—cast irons and steels
	Heavy	Cu Ni Pb Zn Sn Copper, nickel, lead, zinc, tin
	Light	Al Mg Ti Be Aluminium, magnesium, titanium, beryllium, Ca Sr Ba Li calcium, strontium, barium, lithium, Na K Rb Cs sodium, potassium, rubidium, cesium
	Smaller Minor	Co Cd Sb Bi Cobalt, cadmium, antimony, bismuth, Hg As mercury, arsenic
onfer us etals	Noble	Au Ag Pt Os Gold, silver, platinum, osmium, Ir Ru Rh Pd iridium, ruthenium, rhodium, palladium,
	Refractory	W Mo V Ta Ti Tungsten, molybdenum, vanadium, tantalum, titanium*, Nb Cr Mn Zr Re niobium, chromium, manganese, zirconium, rhenium**,
	Rare-earth	Sc Y La Ce Scandium, yttrium, lanthanum, cerium, Pr Nd Sm Eu praseodymium, neodymium, samarium, europium, Gd Tb Yb Dy gadolinium, terbium, ytterbium, dysprosium, Ho Er Tu Lu holmium, erbium, thulium, lutecium

Continued

Group	Subgroup	Metals
Nonferrous metals	Disseminated	Ge Germanium, Ga gallium, Tl thallium, Re (rhenium), Hf hafnium, In indium
	Radioactive	U Uranium, Th thorium, Pa protactinium, Ra radium, Np neptunium, Pu plutonium

* Titanium by its low density (4500 kg/m³) and manufacture in conjunction with magnesium, should be referred to as a light metal, and by its melting point (1655 °C)s as a refractory metal.

** Rhenium is a refractory metal (melting point of 3180±20 °C), but by its occurrence in nature is a typical disseminated element.

sulphides, silicates and other salts. Metals of greater potentials, and, consequently, of lesser chemical activity are the more stable in a free state, the greater their potential. For example, copper, silver and mercury occur naturally not only as salts, but in a free state as well, whereas platinum is found mainly in a native state.

Notice that Table 3 describes the properties qualitatively only. Thus, the rate of oxidation of metals in the air or displacement of hydrogen by them in an acid is affected by the state of their surfaces, which are generally coated with films of oxides or various compounds resulting from interaction with atmospheric gases. Action of acids upon surfaces of metals results in deposition of salts, which are sometimes very poorly soluble in water and thus slow down the reduction of hydrogen ions.

The periodic table of the elements of D.I. Mendeleev gives a clear-cut classification of elements by their chemical properties, but it does not, naturally, describe the particularities of manufacture and application of metals that are produced in large quantities. From this stems a commercial or technical classification, which lacks scientific basis, but is traditionally used in technical literature and industrial practice (Table 4).

Table 5

Physical and Mechanical Properties of Major Metals

Metals	Atomic mass	Density at 20°C, kg/m³	Temperature of, °C		Coefficient of heat conductivity * (at 20°C)		Specific electric resistance at 20°C, ohm·m	Mechanical properties **			
								tensile strength		Brinell hardness	
			melting	boiling	W (m·deg)	cal (cm·s·deg)		N/m²	kgf/mm²	N/m²	kgf/mm²
Heavy											
Copper	63.54	8.960	1083	2600	393.56	0.94	0.018	215.8	22	343.4	35
Nickel	58.69	8.900	1455	2730	92.11	0.22	0.068	441.5	45	686.7	70
Lead	207.21	11.340	327.4	1740	35.17	0.084	0.206	14.7	1.5	49.1	5
Zinc	65.38	7.140	419.5	907	112.23	0.268	0.059	127.5	13	372.8	38
Light											
Aluminium	26.98	2.670	660.2	2060	221.9	0.53	0.026	98.1	10	264.9	27
Magnesium	24.32	1.740	650	1107	159.1	0.38	0.047	176.6	18	245.3	25
Titanium	47.90	4.540	1800	3400	15.9	0.036	0.47	313.9	32	833.9	85
Refractory											
Tungsten	183.92	19.350	3377	6000	167.47	0.4	5.03	343.4	35	2943.0	300
Molybdenum	95.95	10.200	2625	4800	146.54	0.35	0.0517	686.7	70	1226.3	125

* A unit of coefficient of heat conductivity in the system SI is equal to $\frac{1\,j}{1\ deg/m \cdot 1\ m^2 \cdot 1\ s} = 1\ W\,(m \cdot deg)$;

1 cal/(cm·s·deg)=418.68 W/(m·deg).

** Units for measuring mechanical properties of a material are units of stress. In the system SI, the unit of stress is 1 N/m² (Newton per square metre); 1 kgf/mm² = 9.81·10⁶ N/m²=9.8 MN/m² [M is mega (10⁶)].

Iron leads by far all other metals as regards the scale of production and use (Table 1). This underlies the differentiation of all metals into iron bearing, or ferrous ones (iron and its alloys, i.e., cast irons and steels) and into non-iron bearing, or nonferrous, metals. The latter in their turn, are subdivided by common characteristics into groups and subgroups (Table 4). Chief physical and mechanical properties of nonferrous metals are compared in Table 5.

2. Chemical Reactions Used in Manufacture of Metals

As mentioned, most metals occur naturally as compounds, chiefly oxides, sulphides, chlorides and silicates. The aim of metallurgy is to obtain free metals by reducing their natural compounds. Of the many suitable for the above purpose chemical reactions, we shall discuss below those only that are economically advantageous and are employed in metallurgical practice.

Reduction by Carbon or Hydrogen

The most available and cheap reducing agent is carbon which accounts for the bulk of coals. Reduction of a metallic oxide, i.e., lead oxide, by carbon may be written thus

$$PbO + C \rightarrow Pb + CO \qquad (1)$$

Similar reactions proceed from left to right, in the direction of reduction if the strength of the chemical bond between oxygen and carbon is greater than that between oxygen and the metal involved. The strength of chemical bonds is termed affinity, which, in chemical thermodynamics is quantified by the isobaric-isothermal potential, designated by the symbol ΔZ. Isobaric potential is expressed in joules or calories*. Its physical sense is the maximum work which the reaction is capable of performing. This work is conventionally assumed to be negative, and, a negative value of

* The Fifth International Conference on Properties of Steam has established in 1956 the following equivalence ratio between a calorie and a joule: 1 calorie = 4.1868 joules. The use of the calorie and its derivatives is admissible as a temporary measure. According to the SI system of units, the recommended unit of heat is joule.

ΔZ is indicative of the ability of a reaction to proceed spontaneously.

Affinity of an element for oxygen or sulphur (isobaric potential of formation of an oxide or a sulphide) is governed by temperature. This relationship may be expressed by an equation of the form

$$\Delta Z = A + BT \log T + CT + \dots$$

where A, B, C = numerical values, obtained experimentally

T = absolute temperature, °K

The effect of temperature in accordance with the above reactions may be represented graphically in a manner shown in Fig. 3, where the ΔZ is referred to 1 mole of oxygen necessary for the formation of oxide. Let us make use of the diagram to calculate the isobaric potential of reduction of lead oxide by carbon at 800°C according to reaction (1). The reaction is feasible, if it is capable of performing work or, in other words, if its isobaric potential is negative

$$\Delta Z = \Delta Z_{CO} - \Delta Z_{PbO} < 0$$

The feasibility of any other reaction may be similarly determined on the basis of known ΔZ values of the reacting compounds

$$\Delta Z = \sum \Delta Z_{res} - \sum \Delta Z_{init} \qquad (2)$$

where $\sum \Delta Z$ are the sums of the isobaric potentials of the reactants. Lead, carbon and other elements are omitted, since their isobaric potentials are zero ($\Delta Z = 0$). From Fig. 3 we find approximately

$$\Delta Z_{PbO} = -250 \text{ kj}, \quad \Delta Z_{CO} = -400 \text{ kj},$$

$$\Delta Z = -400 + 250 = -150 \text{ kj}$$

The difference is negative, therefore, the reaction is feasible. Let us note that PbO and CO lines intersect in Fig. 3 at a temperature of about 320°C. To the left of the intersect the difference in affinities is positive, and so this point marks the temperature of the beginning of the reduction of lead oxide by carbon. Similarly, intersects of corresponding lines indicate the starting temperature of reduction of

other oxides by carbon. For SiO_2, Al_2O_3, CaO, MgO, the temperatures are higher than 1500°C.

Therefore, one may choose temperatures in such a manner that some oxides are reduced to metals, while others remain unchanged. This is the basis, for instance, of lead smelting

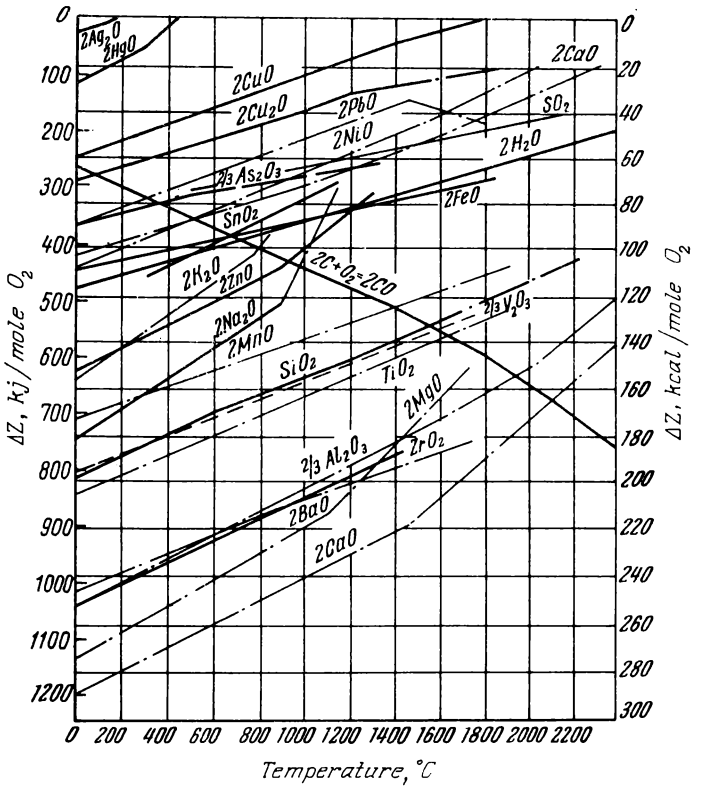

Fig. 3. Standard isobaric potentials of oxide formation

from ores containing SiO_2, FeO, CaO and Al_2O_3. When ores are smelted with use of coke, lead only, of a relatively low affinity for oxygen, is reduced. The oxides that have not been reduced from a molten slag of a density of $\gamma = 3000\text{-}3500$ kg/m^3 which floats over molten lead ($\gamma \approx 10\,000$ kg/m^3), similarly to an oil floating over water.

Of great importance is the rate of reduction. The metallurgical processing stages (conversions) should be highly productive, therefore, the reactions involved should proceed rapidly. Solid state reduction of oxides by carbon is necessarily slow because of a small area of contact of reactants. Contact between even the finest particles of carbon and of an oxide, is quite imperfect, and, what is more, the resultant metal which appears at points of contact puts an end to the reaction by separating the reactants. Solid carbon may be an efficient reducer only if its grains are washed by liquid or vaporous oxides. If the oxides are solid, they are reduced at a faster rate by gaseous carbon monoxide

$$MeO + CO \rightarrow Me + CO_2 \qquad (3)$$

Carbon monoxide may be obtained by the reaction

$$C + CO_2 \rightleftarrows 2CO \qquad (4)$$

In melts whose ability to wet carbon is poor, which are common, particles of carbon are surrounded by a gaseous film of CO and CO_2, and reduction proceeds by way of the reaction (4). The equilibrium constant for the reaction (4) should be written as the ratio of partial pressures of CO_2 and CO. The vapor pressure of carbon, when the latter is in excess, is included by the expression*

$$K_{p(4)} = \frac{P^2_{CO}}{P_{CO_2}}$$

K_p may also be given in a percentage of CO and CO_2 or the content of CO in a mixture of gases, per cent. Let us denote per cent of CO = x; percentage of CO_2 is then $(100 - x)$, and so

$$K_p = \frac{x^2 \cdot 100}{100 - x} \cdot P$$

Thus, the equilibrium constant for the reaction (4) is governed by pressure and temperature. This is evidenced by the data in Fig. 4 obtained from the results of experiments made by Boudouard and Bell.

* Subscript "p" indicates that the equilibrium constant is expressed in terms of partial pressures.

As mentioned, metallic oxides are reduced by carbon monoxide according to the reaction (3) which, if vapor pressures of *Me*O and *Me* are constant, may be written as follows

$$K_{p(3)} = \frac{P_{CO_2}}{P_{CO}}$$

$K_{p(3)}$ may also be represented by the percentage of CO in the gases. If the equilibrium constant for the reactions (3)

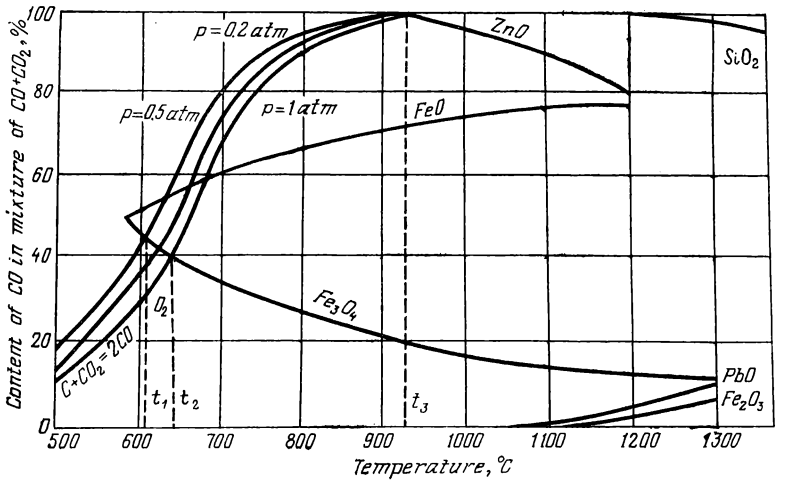

Fig. 4. Reaction equilibrium constant versus temperature

and (4) is plotted versus the temperature in a common system of coordinates, we obtain a diagram which allows to determine the temperature, at which the reduction of metallic oxides begins, as a function of the composition and the pressure of CO and CO_2 (Fig. 4). The reduction is feasible, if $K_{p(4)} > K_{p(3)}$.

It may be seen from the diagram that the temperature of the beginning of PbO reduction is rather low. The same may be said of Fe_2O_3 reducible by the reaction (5).

According to a rule suggested by the academician A. A. Baikov the reduction of higher oxides proceeds in

steps, e.g.

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \quad (5)$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \quad (6)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (7)$$

The reduction of Fe_3O_4 (6) begins at a temperature t_1^0 (close to 600°C) for a total pressure of gases of 0,2 atm. abs. and at t_2^0 (close to 650°C) for $p = 1$ atm. abs. (Fig. 4). Zinc is reducible from temperature t_3^0 (close to 930°C) and higher. Notice that the equilibria of the reactions (5) and (7) call for a greater percentage of CO in the gases than that for the reaction (6).

Both are linked to Le Chatelier's principle which states that an action upon a system in equilibrium gives rise to reactions which tend to counter the former. Reactions (5) and (7) give off heat, and this is why a greater content of the reducer CO is required in the gases. By contrast, the reduction of Fe_3O_4 (6) and that of zinc oxide consumes heat, so that reactions of this type are enhanced by higher temperatures.

Hydrogen is used for reduction of oxides not so often, since it is more costly and explosion-hazardous, but it finds use whenever the formation of carbides is objectionable, i.e., in the reduction of tungsten and molybdenum from oxides according to reactions

$$WO_3 + 3C \rightarrow W + 3CO \quad (8)$$

$$MoO_3 + 3C \rightarrow Mo + 3CO \quad (9)$$

whose by-products are of carbides WC and Mo_2C.

Since many metals occur naturally as sulphides let us evaluate the possibility of reducing them through reaction

$$2MeS + C \rightarrow 2Me + CS_2 \quad (10)$$

by considering Fig. 5 which describes the affinity of elements for sulphur. Carbon is generally a poor reducing agent as regards sulphides. Neither is hydrogen suited for the purpose, since the H_2S line is high, which is indicative of a high degree of improbability of such reactions as

$$MeS + H_2 \rightarrow Me + H_2S \quad (11)$$

In metallurgical practice, natural sulphides are first roasted, i.e., processed to oxides. which are then reduced

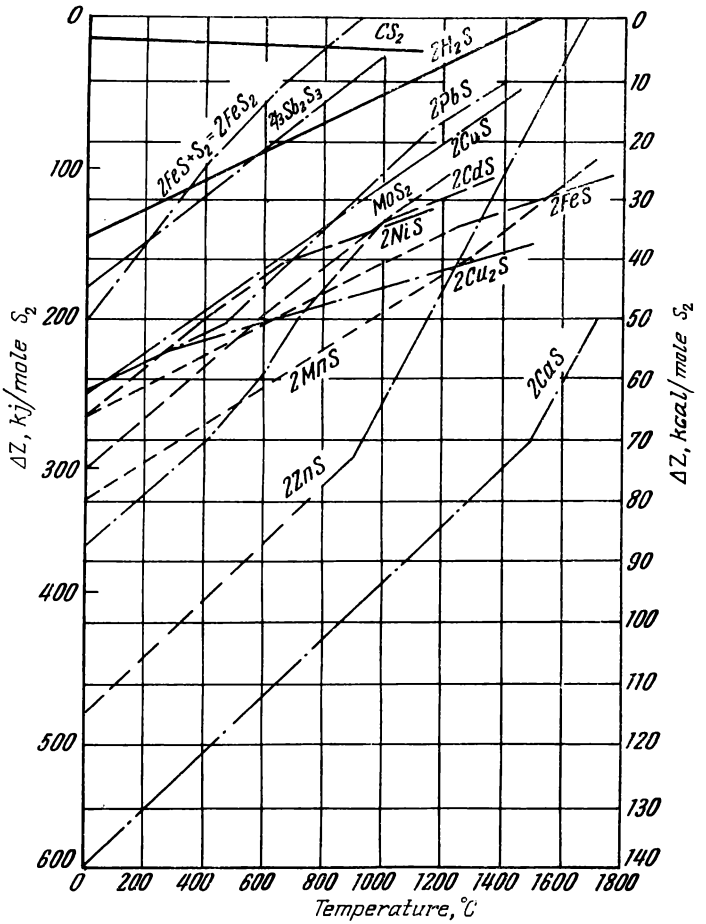

Fig. 5. Standard isobaric potentials of sulphide formation

by carbon. For example, lead sulphide, or galenite, is oxidized by atmospheric oxygen at a temperature of about 1000°C

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \qquad (12)$$

The resultant lead oxide is then reduced by carbon. Zinc is manufactured from its sulphide in a similar manner. Of interest in Fig. 3 is a break in the ZnO line which corresponds to the boiling point of the metal (907°C). Reduced at about 950°C, zinc is in vapours which are exhausted from the furnace, cooled and condensed into liquid or solid metal, depending upon the temperature in the condenser. Notice also that breaks in the lines in Figs. 3 and 5 are indicative of a change in the state, melting or boiling of the metal or its compounds.

Reaction Smelting

This is a method for manufacturing metals through chemical reactions between sulphides and oxides, e.g., between a copper sulphide and cuprous oxide

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2 \qquad (13)$$

Calculation of the isobaric potential of this type of reaction requires the use of diagrams in Figs. 3 and 5. For the temperature of 1200°C, we find

$$\begin{aligned} \Delta Z &= \Delta Z_{SO_2} - 2\Delta Z_{Cu_2O} - \Delta Z_{Cu_2S} \\ \Delta Z &= -250 + 130 + 90 = -30 \text{ kj} \end{aligned} \qquad (14)$$

This technique is sometimes used to reduce lead from its oxide at a temperature of about 800°C. A precondition for the reaction smelting is a relatively small affinity of metals for both oxygen and sulphur.

Electrolysis of Molten Salts

Metals, whose oxides require high temperatures for reduction by carbon or which tend to form carbides, are obtained by electrolysis of molten salts.

Alkali and alkali-earth metals, magnesium and aluminium possess a very great affinity for oxygen, and, at high temperatures they vaporize readily or tend to form carbides. These metals are reduced by electric current from molten salts. The overall procedure may be exemplified by the manufacture of magnesium. First, the source magnesium

carbonate is decomposed

$$MgCO_3 \xrightarrow{1000°C} MgO + CO_2 \qquad (15)$$

resultant magnesium oxide is chlorinated

$$MgO + Cl_2 + C \rightarrow MgCl_2 + CO \qquad (16)$$

and the molten magnesium chloride is treated by electrolysis at about 700°C. When molten, this salt consists of Mg^{2+} and Cl^- ions. At the cathode, magnesium ions acquire two electrons and are thus reduced to metal. The melting point of magnesium is 651°C, and, therefore, it is manufactured in the molten state and because of its lesser density floats over the electrolyte

$$Mg^{2+} + 2e^- \rightarrow Mg \qquad (17)$$

At the positive electrode, the anode, Cl^- ions are oxidized by giving off two electrons, and are thus converted to molecules of gaseous chlorine.

Aluminium is manufactured by electrolysis of its oxide Al_2O_3, dissolved in molten cryolite Na_3AlF_6. In the melt, the Al_2O_3 dissociates at about 1000°C similarly to a salt in water

$$Al_2O_3 \rightleftarrows 2Al^{3+} + 3O^{2-} \qquad (18)$$

Molten aluminium is obtained at the cathode

$$4Al^{3+} + 12e^- \rightarrow 4Al$$

oxygen evolving at the anode

$$6O^{2-} - 12e^- \rightarrow 3O_2$$

Cryolite is merely a dissolving agent, and is not consumed in the electrolysis.

Similarly to the magnesium, alkali metals and calcium are manufactured from chloride and fluoride melts. Reduction of calcium by carbon would have required very high temperatures, in excess of 1800°C (see Fig. 3).

Metallothermics

There is no way for converting some oxides into salts that melt readily and are amenable to electrolysis. At the same time, the oxides may be very stable and irreducible by carbon at convenient temperatures. This is the case with, for examples, titanium tetrachloride $TiCl_4$ and uranium tetrafluoride UF_4, and for oxides of some of the refractory metals, such as V_2O_5, for instance. These compounds can be decomposed by other metals that are cheaper and of a greater affinity for halogens or for oxygen. Titanium is reduced from titanium tetrachloride by magnesium according to reaction

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2 \qquad (19)$$

Uranium, by the use of magnesium or calcium

$$\begin{aligned} UF_4 + 2Ca &\rightarrow U + 2CaF_2 \\ UF_4 + 2Mg &\rightarrow U + 2MgF_2 \end{aligned} \qquad (20)$$

and vanadium, by aluminium

$$3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3$$

Many a similar reaction proceeds with evolution of great amounts of heat, sufficient even for melting such refractory metals as vanadium (1735°C), chromium (1800°C), manganese (1250°C). Hence, the name of the technique, the metallothermics.

A metallothermic reaction may readily be carried out by preparing a fine mixture of reactants and igniting it by means of a special fuse, i.e., from magnesium powder and $KClO_3$. The mixture burns and melts in the process from heat generated by the reaction. This is the autogeneous, or self-sustaining metallothermics, which requires no extraneous heating. When the heat of chemical reaction is insufficient to melt the reactants, additional heat is supplied from outside, and the process is then termed furnace metallothermics.

Metallothermic techniques are very costly. The reduction of one metal requires oxidation of another, and so these methods are used only when no other technique is feasible.

All the above reactions for manufacturing metals call for high temperatures, and the corresponding production steps are termed pyrometallurgical (from Greek *pyr*, a fire).

Fuel, electric power and refractories consumed in smelting metals are often very costly. If metal content in an ore is low, whereas that of impurities, high, pyrometallurgical techniques prove to be costly because large quantities of gangue are to be melted or heated in the process.

Sometimes, pyrometallurgy fails to attain desired goal because of specific properties of raw materials or of metals being recovered. The solution to the problem may then lie in hydrometallurgy processing (from Greek *hydor*, water) whose chief technique is leaching.

Leaching by Water Solutions

Metals may be extracted from ores by treating the latter with dilute acids, bases and other reagents by transferring the metals to solutions in the form of salts. Gangue is left over in the insoluble residue. It is filtered off, whereas metals are settled out of the filtrate by *electrolysis* or *cementation* displacement reaction.

Sometimes the resultant solutions are excessively diluted, and direct recovery of metals from them is disadvantageous. Such solutions are first concentrated by *ion exchange* and *extraction* or *the metal is settled out in the form of a poorly soluble compound.* All this will be dealt with below.

Electrolysis of Water Solutions

Electrolysis is carried out in *electrolytic tanks*, which are vessels, generally prismatic in shape (Figs 37, 38) where *anodes* and *cathodes* are suspended alternately, vertically and parallel to one another. The anodes are connected to the positive and the cathodes to the negative poles of a DC source of electric power. The resultant difference of potentials between the anode and the cathode may be visualized as an excess of electrons at the cathode and their lack at the anode.

In the solution filling the bath, i.e., in the electrolyte, salts of metals are dissociated to ions whose motion is due

to diffusion and stirring only. The electrodes can attract or repulse them at very small distances only, inside a zone near the electrodes whose thickness is measured by a few rows of molecules. The motion of individual ions toward the cathode or anode is the effect of a decrease in their concentrations in the zone near the electrodes.

When near the cathode, the ions that are reducible accept electrons, and if in that their charge falls to zero, they are converted into neutral atoms, e.g., according to the pattern

$$Cu^{2+} + 2\bar{e} \rightarrow Cu^0$$

The neutral atoms, in the present instance those of copper, attach themselves to the cathode to form a crystalline lattice of copper. The result is a gradual build-up of a solid and thick layer of copper. Hydrogen ions that result from the decomposition of acids are reduced to gaseous hydrogen which accumulates in bubbles at the surface that break away after reaching a critical volume and float in the electrolyte*

$$2H^+ + 2\bar{e} \rightarrow H_2 \qquad (21)$$

Ions that are partly reduced generally remain in the solution

$$Fe^{3+} + \bar{e} \rightarrow Fe^{2+} \qquad (22)$$

Cathode and anode are conventional designations and should not be understood as the negative and positive poles of the cell, although the potential of the former is always somewhat more negative than that of the latter. At the same time, both electrodes can be either at positive or negative potentials, and potentials of different signs with respect to the hydrogen electrode**.

It would be also erroneous to assume that cations only discharge at the cathode, and anions, at the anode. Actually, anions are reducible at the cathode. An example is MnO_4^- which does so with formation of ion Mn^{2+} or a deposit of

* It is well to note here that in general electrical engineering the zero charge is considered that of the earth, and in electrical chemistry, that of the hydrogen electrode, which is not in the least equal to zero.

** Actually hydrogen ions are hydrated and their correct designation is H_3O^+, a fact generally overlooked and we shall follow the customary assumption for the sake of simplicity.

$MnO_2 \cdot H_2O$.

$$MnO_4^- + 8H^+ + 5\bar{e} \rightleftarrows Mn^{2+} + 4H_2O; \quad E^0 = 1.52 \text{ V}$$

$$MnO_4^- + 4H^+ + 3\bar{e} \rightleftarrows MnO_2 \cdot H_2O + H_2O; \quad E^0 = 0.59 \text{ V}$$

Often oxidized at the anode are cations

$$Fe^{2+} - \bar{e} \rightleftarrows Fe^{3+}; \quad E^0 = 0.77 \text{ V} \tag{23}$$

or molecules of water

$$2H_2O - 4\bar{e} \rightleftarrows 4H^+ + O_2; \quad E^0 = 1.23 \text{ V} \tag{24}$$

It would be wrong to assume that OH^- ions discharge from acid solutions at the anode. Their activity is always below 10^{-7} milligrams per litre and could never account for a violent evolution of oxygen which is sometimes the case, although, to judge by the normal potential value, their discharge would seem to be preferable to the oxidation of water

$$4OH^- - 4\bar{e} \rightarrow O_2 + 2H_2O \; ; \; E^0 = 0.40\text{V} \tag{25}$$

Electrolysis should be taken as an oxidation-reduction reaction which is the effect of work performed by electric current. Some substances are reduced at the cathode, while others are oxidized at the anode.

Should an electrolyte contain a number of oxidizers, the first to be reduced at the cathode will be the strongest one. In a solution containing monomolecular activities* of copper and silver, silver will be reduced first (Table 2). At the beginning, the potential of the cathode is very close to 0.8 V, but as silver is deposited at the cathode and its activity in the electrolyte decreases, the potential varies

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* Activities of ions in electrolytes are fractions of their total concentrations that are capable of interacting chemically, or $a = f \cdot c$, where f is the activity coefficient, which is governed not by concentrations of the given ions solely, but by the amounts of other ions present in the electrolyte, or by the ionic power of the solution, c is concentration in moles per litre. In very diluted solutions $f \approx 1$, $a \approx c$.

in accordance with Nernst's equation*

$$E_{Ag^+/Ag} = E^0_{Ag^+/Ag} + \frac{RT}{nF} \ln a_{Ag^+} = 0.80 + \frac{0.06}{n} \log a_{Ag} \quad (26)$$

Copper may be deposited simultaneously with silver only when $E_{Ag^+/Ag} = 0.34$ V, i.e., when the activity of silver falls to

$$\log a_{Ag^+} = \frac{0.34 - 0.80}{0.06} = -7.7 a_{Ag} =$$

$$= 2 \cdot 10^{-8} \text{ gram-ion/l} \approx 2 \cdot 10^{-6} \text{ g/l}$$

On the face of it, cathodic deposition from acid solutions of metals of negative potentials may seem impossible, since $E^0_{2H^+/H_2} = \pm 0.00$ V (Table 2), and hydrogen should evolve at the cathode first. In practice however, not only nickel, cobalt, cadmium and iron, but even zinc and manganese (although $E^0_{Zn^{2+}/Zn} = -0.76$ V and $E^0_{Mn^{2+}/Mn} = -1.1$ V) can be settled out by electrolysis. This is favoured by a low rate of reduction of ions (due to gases being given off) which proceeds in stages. The main of these are attachment (adsorption) of ion H^+ to the surface of the cathode, the ion's discharge with formation of atomic hydrogen, combination of two atoms into a molecule H_2, destruction of the bond to the cathode (desorption) and accumulation of the gas into bubble. One of the stages, the slowest one, determines the rate of the whole chain of transformations, the rate differing with the metal of the cathode. The discharge of ions of metals is also a multi-stage process, but in general it is fairly rapid, although there are exceptions, as, the discharge of iron, cobalt and nickel. The above points to a conclusion that a possibility of discharge of ions with the formation of a gas is determined not only by the equilibrium potential value, but also by an overvoltage. The latter is a negative value, or polarization of the cathode, by which the equilibrium potential of the cathode should be exceeded to allow evolu-

* Here: R = gas constant, equal to 8.314 j/deg
T = absolute temperature which is arbitrarily taken to be 303°K, or 30°C
n = number of electrons participating in the reduction
F = Faraday's number, equal to 96 500 coulombs
In the calculation, use has been made of the modulus for converting natural logarithms into common ones, $m = 2, 3...$

tion of bubbles of gas. Specifically, for hydrogen it is

$$E_{H^+} = E^0_{2H^+/H_2} + 0.06 \log a^2_{H^+} - \eta = 0.06 \log a^2_{H^+} - \eta \quad (27)$$

Overvoltage (η) depends on the material of the cathode, it decreases as temperature rises and increases with *current density* (D). The latter is the intensity of current in amperes per unit area of electrode expressed in A/m², A/dcm² or A/cm².

The relationship between the hydrogen overvoltage and the current density is given by Tafel's equation

$$\eta = a + b \log D_c$$

where η = overvoltage, V
D_c = cathode current density, A/cm²
a and b = factors that depend on the material of cathodes and the temperature

Potentials of cathode reduction of some metals and hydrogen from solutions with the activities a_{H^+} and $a_{Me^{n+}}$ taken to be 1 mole per litre and 0.01 mole per litre are compared in Table 6. These activities are conventionally

Table 6

Potentials Reducing Hydrogen and Some Metals from Solutions Activities a_{H^+} and $a_{Me^{n+}}$ of 1 g-ion/lit and 0.01 g-ion/lit. Respectively at 20°C and Current Density of 100 A/m²

Metal	Reduction potential of H+, V		Reduction potentials of metals, V	
	a=1 g-ion/l	a=0.01 g-ion/l	a=1 g-ion/l	a=0.01 g-ion/l
Al	—0.83	—0.95	—1.66	—1.70
Cu	—0.56	—0.68	0.34	0.28
Hg	—1.17	—1.29	0.79	0.73
Ag	—0.71	—0.83	0.80	0.74
Pb	—1.34	—1.46	—0.13	—0.19
Ni	—	—	—0.25	—0.31
Co	—0.34	—0.46	—0.34	—0.45
Cd	—1.16	—1.28	—0.40	—0.46
Fe	—0.44	—0.56	—0.44	—0.50
Zn	—1.00	—1.12	—0.76	—0.82

referred to the beginning and the end of electrolysis: for $a_{H^+} = 1$ g-ion/l, $E_{H^+} = -\eta$ (27); and for $a_{H^+} = 10^{-2}$ g-ion/l, $E_{H^+} = 0.06\ (-2) - \eta = -0.12 - \eta$, V.

Potential of reduction of aluminium is by far more negative (Table 6) than that required for the evolution of hydrogen. The difference is fairly great and it cannot be eliminated by increasing the concentration of Al^{3+} or decreasing the acidity of the electrolyte. Feasible decrease in the temperature or increase in the current density proves to be inadequate as regards the raise of hydrogen overvoltage with respect to aluminium. Whatever the conditions, the electrolysis of a water solution of an aluminium compound yields hydrogen only at the cathode. The effect is the same, if solutions of alkali or alkali-earth metals are subjected to electrolysis since the oxidation-reduction (redox) potential of these elements is more negative than that of aluminium.

By contrast, electrode potentials of copper, mercury and silver are much more positive than the hydrogen overvoltage, and these metals can readily be reduced by electrolysis from even very diluted acid solutions.

Electrode potentials of lead, cadmium, zinc and other elements are a trifle quantity greater or lesser than E_{H^+}, and sometimes their ratio is affected by concentrations. Cathodic reduction is feasible in this case, if the amount of ions Me^{n+} in the solution is not too small and the acidity is below a predetermined level. The reduction is sometimes aided by greater current density and cooling of electrolyte, both these factors increasing hydrogen overvoltage.

Combined deposition of several metals is the chief cause of contamination of cathodic deposits. Contamination is possible not only when electrode potentials are equal, but may also be the effect of *concentration polarization* which will be discussed below.

In a thin layer of electrolyte near the cathode, where the forces of attraction securely hold the contiguous molecules, ions move only through *molecular diffusion*, stirring having no effect whatsoever. The rate of diffusion is expressed by the equation describing Fick's law

$$V = \frac{dm}{dt} = D \cdot S \cdot \frac{C_1 - C_2}{\delta} \qquad (28)$$

where $V = \frac{dm}{dt}$ = speed of motion of ions toward the electrode in g-ions per second

S = surface area of electrode, cm^2

C_1 and C_2 = concentration of the substance being transported within the limits of the by-electrode layer, g-ions per cubic centimetre

δ = thickness of the by-electrode layer, cm

D = coefficient of diffusion of the given ion, cm^2/s

In the course of electrolysis, the concentration of the substance being deposited at the cathode (C_1) decreases as does the rate of diffusion, whereas the quantity of electrons coming to a unit surface area of cathode from the external circuit (a function of current density) remains constant. Excess electrons accumulate at the cathode, and its potential becomes more negative. The resultant *concentration polarization* may cause co-deposition of impurities whose oxidation-reduction potentials are less than that of the base metal.

The current that corresponds to the rate of diffusion is termed the *diffusion current*, whereas that exceeding it, the *limit current*. This latter condition is considered to be the chief cause of contamination of cathodic deposits, and is generally described as deposition of impurities at limit current. Other causes related to a possibility of formation of alloys or entrapment of electrolyte by the growing deposit of metal are discussed below in Paras 19 and 26.

Reduction at the cathode is always paralleled by the oxidation at the anode of a substance which transmits a required amount of electrons to the external circuit. First oxidized are the strongest reducing agents whose oxidation-reduction potentials are most negative. The substance may happen to be the metal of the anode which then oxidizes, as, copper in acid solutions, according to the reaction

$$Cu - 2\bar{e} \rightarrow Cu^{2+}$$

The anode passes into the solution in the process, whereas the metal is reduced again at the cathode. *Electrolysis with a soluble anode* is used to refine metals. If the metal of the

anode does not pass into the solution, e.g., lead, which combines with sulphuric acid to give an insoluble salt $PbSO_4$, the anode *passivates* due to the formation on its surface of a deposit of lead sulphate with the effect that the anode's active surface area gradually decreases and concentration polarization sets in. Electrons pass from the anode into the external circuit with no replacement electrons coming from the electrolyte, and the anode's potential grows more and more positive. Once it reaches a value sufficient for oxidation of another less strong reducing agent, water, oxygen evolves according to the reaction (24).

Similarly to other gases, oxygen evolves at an overvoltage which has a positive sign at the anode. Anions of strong acids are not generally oxidized at the anode, since the necessary potentials are too high

$$2Cl^- - 2e^- \rightleftarrows Cl_2 \quad ; \quad E^0 = 1.36 \text{ V} \tag{29}$$

$$2SO_4^{2-} - 2e^- \rightleftarrows S_2O_2^{2-}; \quad E^0 = 2.01 \text{ V} \tag{30}$$

The passivated lead anode may also be the site of the reaction

$$PbSO_4 + 2H_2O - 2e^- \rightleftarrows PbO_2 + 4H^+ + SO_4^{2-} \tag{31}$$

The consumption of electric power in electrolysis is calculated in kW·h per ton of deposited metal

$$W = K_{ce} I \cdot V \tag{32}$$

where W = consumption of electric power, kW·h
I = current intensity, A
t = time, h
V = voltage across the bath, Vt
K_{ce} = a factor that indicates what fraction of the current is utilized for the deposition of the metal, or *current efficiency*, fraction of a unit or per cent

A fraction of current, equal to $(1 - K_{ce})$ is consumed for the combined deposition of impurities or lost in stray circuits, as due to poor insulation of the bath from the earth. The voltage across the bath may be generally expressed by the equation

$$V = E_a - E_c + IR \tag{33}$$

where E_a and E_c are the potentials of the anode and the cathode, respectively, which add up of equilibrium values that, in their turn, depend on the activity of the discharging substances and the temperature and are the potentials necessary to overcome the concentration and the chemical polarizations (overvoltages). The latter are governed by the temperature, current density, stirring and the nature of the metal being deposited. More than that, the possibility that several substances may discharge at the electrodes in one operation, makes the calculation of E_a and E_c still more intricate. Generally, electrode potentials are found by calculating the loss of voltage IR, where I is the current in amperes, and R, the electrical resistance of the bath circuit in ohms, which includes the resistance of the electrolyte, and that of the electrodes and their connections to the external circuit. All that has been said on the electrolysis of water solutions holds true for molten salts which, however, should contain no hydrogen ions. The absence of the latter ions is essential to the cathodic deposition of magnesium, aluminium, alkali and alkali-earth metals, as has been mentioned before.

Cementation

Cementation is a displacement of a metal by another from an aqueous solution or a melt, e.g., according to the reaction

$$Cu^{2+} + Fe^0 \rightleftarrows Cu^0 + Fe^{2+} \qquad (34)$$

Similarly to the electrolysis, this is also an oxidation-reduction process, effected not by an electric current, but selfsustained and capable of generating electric power, the same as a galvanic cell. Reaction (34) is made up of two oxidation-reduction systems 13 and 7 (Table 3). If electrons can be transmitted from iron to copper, the effect is a galvanic cell whose electromotive force equals

$$E^0 = 0.34 - (-0.44) = 0.78 \text{ V}$$

Index zero, the same as above, indicates standard conditions, i.e., equality of activities

$$a_{Cu^{2+}} = a_{Fe^{2+}} = 1 \text{ g-ion/l}$$

Positive value E^0 is the first necessary, but insufficient, precondition of the feasibility of similar reactions which go out slowly because of low rate before an equilibrium is reached. Fig. 40 illustrates schematically the interaction of an iron particle with a solution of a copper salt in which it is immersed. Discharge of copper ions begins at the most active areas of the particle where there is an excess of surface energy and, therefore, adsorption is favoured. Nuclei of crystals grow in size, receive and run off charges of ions, a system of galvanic cells resulting, the anode being commonly iron, and the cathodes, crystals of copper.

Should for any reason, e.g., oxidation or any other adverse effect upon the surface, the growth of the previously formed crystals cease, ions will find new centres upon the particle of iron that are capable of forming fresh nuclei. The total surface area of copper cathodes will then increase, and conversely, the surface area of iron will decrease as will the passing of iron ions to the solution.

A formula for calculating the equilibrium constant of an oxidation-reduction reaction can readily be derived from Nernst's equation. This formula holds for the case in hand

$$\log K = \frac{E^0_{ox} - E^0_{red}}{0.06} \cdot n$$
$$pK = \frac{E^0_{red} - E^0_{ox}}{0.06} \cdot n \qquad (35)$$

Therefore,

$$K = \frac{a_{Fe^{2+}}}{a_{Cu^{2+}}} = 10^{26}$$

Assuming at the end of settling $a_{Fe^{2+}} = 1$ gram-ion/litre, we obtain the equilibrium residual concentration of copper

$$[Cu^{2+}] \approx a_{Cu^{2+}} = 10^{26} \text{ g-ion/lit} =$$
$$= 10^{-26} \cdot 63.54 \approx 6.3 \cdot 10^{-25} \text{ g/lit } Cu^{2+}$$

Actually, so high a cementation is never attained, since it ceases after copper crystals cover all of the free surface areas of iron particles. This comes about the earlier, the faster the appearance of new centres of crystallization and

the slower the growth of crystals already formed, the contributing factors being low temperatures and high concentrations of the metal being deposited.

The consumption of the settling metal is always higher than the stoichiometric amount, chiefly because of the deposit that covers its surface and prevents interaction with the solution. In solutions of higher acidities, oxidation and contamination of the surface of cathodic areas is less probable. Along with this, the acid, with the participation of atmospheric oxygen, dissolves the deposit

$$Cu + O_2 + 4H^+ \rightarrow Cu^{2+} + 2H_2O \qquad (36)$$

An alternative oxidation of copper is also possible

$$4Fe^{2+} + O_2 + 4H \rightarrow 4Fe^{3+} + 2H_2O$$

In either case, iron is consumed inefficiently. In addition, it dissolves directly in the acid to yield hydrogen

$$Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} \qquad (37)$$

The latter sometimes may have a favourable effect: bubbling hydrogen tears off copper deposits and contributes to its loosening and separation. The rate of a cementation initially corresponds to the rate of delivery of copper ions by diffusion as described by the equation (27). However, as the free surface of the settling agent decreases, the rate is being more and more governed by a similar diffusion run off of Fe^{2+} ions through passages and pores between crystals of copper. Calculations by the use of equation (27) are made difficult by the absence of data on the continuously varying free surface area of iron, the deposit often cracking and peeling off it. Another factor that slows down diffusion of Fe^{2+} ions is their high concentration (28). The finer a settling agent and the greater its total surface area, the faster and the more complete is a cementation. The latter can often be speeded up by artificial stripping of the deposit off the settling agent particles, e.g., in ball mills or by any alternative means.

Reduction of Metals from Solutions by Hydrogen or Other Gases

Solubility of hydrogen and other gases in metals is dependent upon the nature of the metal and the size of its particles.

If all this takes place in a solution, at the interface with the metal, an oxidation-reduction potential is generated. For hydrogen, it may be expressed by a system

$$H_2 - 2\bar{e} \rightleftarrows 2H^+; \quad K = \frac{a^2_{H^+}}{p_{H_2}} \tag{38}$$

Making use of Nernst's equation, with $E^0_{2H^+/H_2} = 0$, we find

$$E_{2H^+/H_2} = \frac{RT}{nF} \ln \bar{K} = \frac{0.06}{2} \log \frac{a^2_{H^+}}{p_{H_2}} \tag{39}$$

where K = equilibrium constant

$\bar{K}$ = is the ratio corresponding to K* in form but written with the starting instead of the equilibrium concentrations. The temperature, as before, is assumed equal to 30°C, and it is described by the coefficient $\frac{0.06}{2}$ which precedes the logarithm

Assuming $p_{H_2} = 1$ atm and $a_{H^+} = 10^{-7}$, we have

$$E_{2H^+/H_2} = -0.42 \text{ V}$$

From the above simplified calculation, it becomes readily apparent that the hydrogen electrode potential is sufficient to reduce copper according to the reaction below, but it falls off rapidly as ions H^+ accumulate in the solution

$$Cu^{2+} + H_2 \rightarrow Cu^0 + 2H^+ \tag{40}$$

$$K = \frac{a^2_{H^+}}{a_{Cu^{2+}}} = 10^{\frac{0.34-(-0.42)\cdot 2}{0.06}} \approx 10^{25}$$

* Activities of oxidizers are always written as numerators in equations describing oxidation-reduction systems.

A more correct approach would be to take into account both the fugitivity of gases, which is similar to activity of ions in water solutions, and the coefficient of fugitivity, which depends on pressure.

Copper, nickel and cobalt can be reduced from their compounds, similarly to hydrogen reduction, by the action of carbon monoxide and sulphurous gas whose oxidation-reduction properties can be described by the system below

$$CO + H_2O - 2e^- \rightleftarrows CO_2 + 2H^+ \quad (41)$$

$$SO_2 + 2H_2O - 2e^- \rightleftarrows SO_4^{2-} + 4H^+ \quad (42)$$

The rate of cementation by gases is low at usual temperatures and pressures, but rises sharply with increases in them. It is a common fact that water solutions cannot be heated to temperatures much higher than 100°C since they boil. For this reason, metals are reduced from solutions by gases in thick-walled air-tight metallic autoclaves which also allow a raise in the pressure of the reducing gas. Boiling points of water and its solutions rise with the pressure, and the values for water, which also hold for aqueous solutions after minor corrections, are as follows:

p, kN/m² (atm) . .	98.1(1)	598.6(6)	981(10)	1580(16)	1962(20)
T_b, °C	100	159.2	180.3	201.9	213.0

3. Ores and Ore Deposits

Metals are manufactured chiefly from ores*, and the ores are mined from the earth. The Earth's crust is built of various rocks composed of minerals, which are chemical compounds, solid solutions and other substances formed of chemical elements by natural geochemical processes.

Most of minerals are solid crystalline substances. They differ in composition, colour, lustre, density, hardness and other characteristics. Depending on composition, minerals are divided into oxides, sulphides, silicates and other types. For example, chalcopyrite $CuFeS_2$ is referred to sulphides; smithsonite $ZnCO_3$, to carbonates; kaolinite $Al_2O_3 \cdot 2SiO_2 \times \times 2H_2O$, to alumosilicates. Native minerals, represented by free elements or their alloys, i.e., native copper, native gold and platinum alloys with other metals, native sulphur, are not a frequent occurrence.

* Partly also from processing of waste and scrap.

Rocks are but rarely simple mixtures of minerals. They are mostly stone-like masses in which some minerals are included or finely distributed (ingrained) in others.

Ores are rocks that can be efficiently processed to metals by techniques currently available. A first measure of such an evaluation is the percentage of the values in an ore. It is complemented by calculating the cost of mining, transportation and processing.

Ores are named after metals that are extracted from them, e.g., copper, lead, nickel ores, and, additionally, by the predominating type of mineral: sulphide, oxide, native. Ores that serve for the manufacture of several metals are termed complex (less frequently, polymetallic) ores, e.g., lead-zinc, copper-nickel ores, etc.

Minerals containing values that are extractable by a complex processing are considered ore minerals, and those of no value, gangue. The difference between the both is arbitrary. It depends on the level of processing techniques and the efficiency of complex recovery. As metallurgical production processes are being continually perfected, less and less gangue minerals remain worthless.

Metals are distributed unevenly in the earth's crust. They have accumulated at some locations and formed ores, thus giving rise to ore deposits. Average contents of metals in the earth's crust are quite small. This follows from Table 7 where they are given in per cent of the weight of earth's crust down to a depth of 16 km. Comparison, for example, of the average content of copper in ores (approximately equal to 1%) with its content in the earth's crust supplies conclusive evidence that ore deposits are not frequent.

Having found an ore, geologists prospect the deposit, i.e., determine the quality of the ore and its resources. Should the latter be sufficiently great so as to justify the building of a mining and metallurgical enterprise, the deposit is worked.

Sometimes ores occur at a small depth, and they can be then mined by the relatively cheap open-pit techniques with the use of power shovels, bulldozers, monitors and other mechanisms. Not uncommonly, the deposits are very deep, and the ore is then mined by more complicated and costly underground methods involving the building of mines.

Table 7

Average Content of Metals in the Earth's Crust, % by Mass

1—10	10-1—1	10-2—10-1	10-3—10-2	10-4—10-3	10-5—10-4	10-6—10-5	10-7—10-6	10-10—10-9
Al	Ti	Ba	Rb	Sc	Sb	Hg	Au	Ra
7.45	0.60	0.05	$8 \cdot 10^{-3}$	$6 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-6}$	$5 \cdot 10^{-7}$	$2 \cdot 10^{-10}$
Fe	Mn	Sr	Li	As	Nb	Pd	Re	
4.20	0.10	0.035	$5 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$3.2 \cdot 10^{-5}$	$5 \cdot 10^{-6}$	10^{-7}	
Ca		Cr	Y	U	Ta	Rn		
3.25		0.03	$5 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	$5 \cdot 10^{-6}$		
Na		Zr	Sn	Be	Pt	Os		
2.40		0.025	$8 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-6}$		
K		V	Co	Cd	Ag	Rh		
2.35		0.02	$2 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	10^{-5}	10^{-6}		
Mg		Ni	Th	Hf	Tl	Se		
2.35		0.02	10^{-3}	$4 \cdot 10^{-4}$	10^{-5}	10^{-6}		
		Zn	Pb	Ge	Be			
		0.02	$1.6 \cdot 10^{-3}$	10^{-4}	10^{-5}			
		Cu	W	Ga	In			
		0.01	$7 \cdot 10^{-3}$	10^{-4}	10^{-5}			
		Rare-earths	Mo					
		0.01	10^{-3}					
			Cs					
			10^{-3}					

Metallurgical plants are generally located near deposits so as to avoid transportation of ores over great distances, but this is not always possible because of, for example, lack of local fuel, severe climatic conditions and for many other reasons.

4. Ore Dressing

A saving on the auxiliary materials, fuel, electric power, fluxing agents can be effected, when processing an ore, high in gangue to metal, by removing the latter wholly or partly with the aid of techniques that are cheaper than metallurgical processing and that require no change in the chemical composition or the state of aggregation of the minerals. The methods for pre-conditioning ores, based on differences in properties of minerals such as colour, lustre, density size, magnetic susceptibility, wettability by water, electri

conductivity and other physical particularities of minerals, are termed ore dressing, or beneficiation.

The simplest, although outdated today, is picking of ore by colour and lustre.

Minerals in lumps of ore are often intermixed, intergrown or finely ingrained into one another, and these ores can be dressed only after they have been crushed and reduced to a size that allows separation of individual minerals whose concretions have been broken apart. Over-grinding is undesirable as differences in physical properties of fine particles are less apparent.

After crushing and grinding to required size, ore is beneficiated by one of the techniques below:

1. Manual picking of ore by colour, lustre and shape of lumps of minerals directly at the working faces or on conveyors. Picked are large lumps of rich ore or gangue.

2. Beneficiation by hardness, brittleness and shape of lumps of minerals based on differences in grindability of minerals. Subsequent screening separates crushed ore to concentrate and tailings.

3. Electrostatic beneficiation is based on differences in electric conductivity, electric capacitance and dielectric properties of minerals.

4. Magnetic, or specifically electromagnetic, separation is the separation of minerals by magnetic properties.

5. Gravity concentration makes use of differences in densities and rates of fall of grains of minerals in liquids or in the air.

6. Beneficiation in heavy media is a separation of minerals by densities in a heavy liquid or suspension (medium). In a given medium, some minerals float while others sink. The heavy media are organic liquids, solutions or suspensions.

7. Flotation is based on different wettability of surfaces of minerals by water after ores are treated by flotation agents.

Of the above beneficiation techniques, ores of nonferrous metals are mostly treated by flotation, gravity and magnetic methods. Beneficiation results in the separation of ore into a concentrate and tailings respectively rich and lean in metal. Concentrate is processed to metal, whereas tailings

are dumped unless they present a value from the standpoint of other industries.

A perfect separation of ore minerals and gangue is impossible because of intergrowths remaining even in the smallest of grains, insufficient differences in physical properties of minerals and for a host of other reasons. The concentrate carries some gangue, and the tailings, some metal. Beneficiation results may be described by a ratio of percentages of the metal in the concentrate and in the ore, or the beneficiation ratio. Another major characteristic is the recovery, which is the ratio of the amount of a metal in a concentrate to that in the processed ore, expressed as a fraction of unity or in per cent.

For example, if a 1% copper ore is processed to a 30% copper concentrate, the beneficiation ratio is 30, one ton of ore then yielding 30 kg of concentrate. Let us calculate the recovery:

amount of copper in the ore

$$\frac{1000 \cdot 1}{100} = 10 \text{ kg}$$

amount of copper in the concentrate

$$\frac{30 \cdot 30}{100} = 9 \text{ kg}$$

The recovery then is

$$E = \frac{9}{10} = 0.9, \text{ or } 90\%$$

Sometimes beneficiation yields a third product, generally termed middlings. It is lower in base metal than the concentrate, but higher than the tailings. It is treated separately from the concentrate, special techniques being usually more economically attractive.

Complex ores which carry two or three ore minerals are selectively beneficiated to extract each ore mineral to an individual concentrate. For example, copper-lead-zinc ores are processed to copper, lead, zinc concentrates, middlings and tailings. Each of the concentrates is treated then separately to corresponding metal.

Ore dressing not only simplifies ore processing and lowers its cost, but contributes to the expansion of commercial ore reserves as well. Lean rocks that formerly were not considered ores because of a low content of metals (and, therefore, were not processed) are currently being beneficiated. In the last century, rocks with less than 1% copper were not classed with the ores and no copper was smelted from them because of the high costs involved. Today, rocks with as low as 0.5% Cu are not infrequently beneficiated and processed to metal.

Selective beneficiation contributes greatly to an economically advantageous complex utilization of ores.

Regretfully, not all ores are amenable to beneficiation, and such hard-to-treat ores are directly processed by metallurgical techniques.

5. Metallurgical Processing of Concentrates and Ores

To win a metal from a concentrate or ore, it is necessary not only to decompose an ore mineral and reduce the metal it contains, but also to separate the metal from gangue and impurities, the necessary chemical and physical treatments being termed metallurgical processes. Generally a metal is obtained by a succession of metallurgical treatments which make up the manufacturing technique, or production process for this metal.

After a metallurgical process, the material being treated separates into several mutually immiscible and readily separable phases, solid, liquid or gaseous, e.g., metal, slag and gases. The metal and slag separate into layers by their densities, while the gases are exhausted. Metals to be extracted are concentrated in one of the phases, impurities passing to other phases. Ready separation of phases is an essential precondition for a successful metallurgical processing.

There are three varieties of pyrometallurgical processes: roasting, smelting and distillation.

Roasting is heating of raw ore or other material to a temperature insufficient for its melting, but adequate to cause changes in the chemical composition of minerals and to remove impurities with the gases. For example, roasting of galenite (12) converts it to lead oxide which can readily be reduced to metal by carbon.

Roasting of tungsten anhydride in a hydrogen current yields tungsten powder

$$WO_3 + 3H_2 \rightarrow W + 3H_2O \quad (43)$$

Roasting combined with sintering, or agglomeration, is intended to pelletizing powder material at temperatures sufficient to melt a lowest-melting component only.

Droplets of the low-melting component wet adjacent particles and solidify when cooled to cement them firmly together, a powder material being thus transformed into a strong porous cake (agglomerate). Sometimes the mutual bonding of solid substances results from their recrystallization. Sintering may be paralleled by an oxidizing or a reducing roasting.

Characteristic of *smelting* is a complete or almost complete melting of raw materials into mutually immiscible products of different densities. These may be two liquids or a liquid and a solid substance that either floats or sinks in the melt. The example of a reducing smelting of lead ore has been discussed previously.

Distillation is a technique for separating a metal and impurities, based on different pressures of vapours of metals and their compounds. Vapours are drawn off and condensed as a liquid or a solid product. In distillation, both the vaporizer and the condenser contain each two readily separable phases, one of these being vapours and gases, and the other, solid or liquid substance.

Heating with carbon of a zinc ore, containing ZnO, Fe_2O_3, SiO_2 and other oxides, results in vapours of zinc since it boils at 907°C, whereas most of the companion metals and oxides are non-volatile

$$ZnO + C \rightarrow Zn\ (vapour) + CO$$

Liquid zinc is obtained by cooling gases containing vapours of zinc.

There are three hydrometallurgical processes: leaching, extraction and precipitation of metals or their compounds out of solutions.

Leaching is selective dissolution of ore minerals in acids, alkalis or solutions of other chemical reagents, conditions being adjusted in a manner to leave a maximum of gangue

in the insoluble residue. The liquid phase, or the solution, is separated from the solid insoluble residue by settling, filtration and washing, and, infrequently, centrifuging.

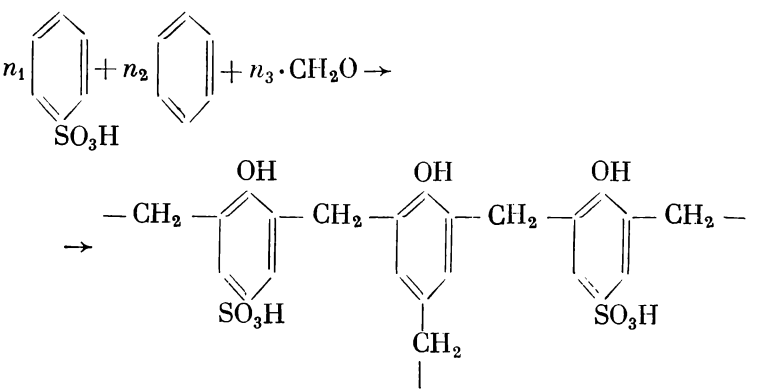
Precipitation of metals or their compounds out of solutions is feasible by a number of methods: electrolysis, cementation or formation of insoluble compounds with corresponding agents. The deposit is again dissolved in a lesser volume of solvent or dried and reduced by pyro-techniques.

Crystallization as well is referred to precipitation methods.

Extraction, the treatment of solutions prior to precipitation is essential when the solutions are lean in metal. The techniques used to this end are ion exchange, coprecipitation, evaporation, etc.

Ion exchange is based on sorption of ions of metals in solution by granular synthetic resins, ionites. Resins that absorb anions only are known as anionites, and those that absorb cations, cationites.

Both these types of ionites are obtained by polymerization or polycondensation of simple organic compounds and introduction into the resultant complicated cellular structure of ion-exchange groups. The simplest example is the polycondensation of a mixture of phenolsulphonic acid and phenol with formaldehyde.



The structure of this polymer may be continued no matter for how far in the direction of free bonds. It is designated by letter *R* for short, with the ion-exchange sulpho-group

SO_3H being shown separately. The resultant cationite is capable of exchanging hydrogen for cations in a water solution

$$mR-SO_3H+Me^{m+}\rightleftarrows mH^{+}+(R-SO_3)\,mMe$$

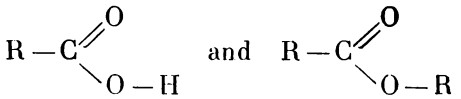
In weak acid solutions, the reaction proceeds from left to right, ions of metal being absorbed by the resin. After all of the values are extracted, the waste solution is separated and dumped, while the *loaded* resin is acted upon by a relatively small quantity of acid. The reaction now proceeds to the left, the metal is obtained as a concentrated solution, an eluate, while the resin becomes once again ready for sorption. Other cationites contain carboxyl ion-exchange group COOH, phosphinous $\begin{matrix}\diagup OH\\ P\\ \diagdown OH\end{matrix}$ or other types of groups. Some cationites are bifunctional, i.e., they have two different ion-exchange groups.

Anionites, with ion-exchange amino-groups of various displacement = N—N; —N=N—; N≡N; —N^+—, absorb anions, inclusive of negatively charged complexes of metals, e.g., $An(CN)_2^-$, $FeCl_4^-$ and others. Resin is regenerated by displacing ions it has absorbed by means of solutions of soda, sodium nitrate and other salts.

To concentrate extracted values, the solution is stirred with an organic solvent and a complex-forming agent which is capable of combining into a complex with the required metal compounds that are better soluble in a given organic liquid than in water. Sometimes the complex-forming agent and the solvent are one and the same substance. By subsequent settling the mixture is separated into two layers, a water one and an organic one. The compounds of the required metal pass chiefly into the organic phase, which is separated and then washed to recover the values by a relatively small volume of an acid or a salt solution. A few subsequent stages of extracting operation allow a practically complete recovery of a metal out of a lean solution and its transfer to a lesser volume, i.e., its concentration.

Complex-forming agents for cations are chiefly organic substances, high-molecular carboxylic acids and ethers which

may generally be represented respectively as



Complex-forming agents for anions are the amins Commonly, the diluent is kerosene, a cheap and effective solvent for non-polar compounds.

Evaporation of solutions aimed at raising their concentration requires no explanation. It should be noted, however, that the method is always costly because of high consumption of fuel.

Modern techniques for manufacturing metals are often complicated and involve a succession of pyrometallurgical and hydrometallurgical processes.

6. Metallurgical Fuel

High temperatures necessary for many pyrometallurgical processing stages are attained through combustion of fuel or, a less frequent practice for the time being, through electric heating.

Fuels are combustible substances advantageously burned to produce heat. They may be solid (coal, peat, wood, coke), liquid (petroleum, fuel oil, kerosene, gasoline) or gaseous (natural and other combustible gases).

A fuel always comprises combustible components such as carbon, hydrogen, hydrocarbons, e.g., methan CH_4 and others that are described by a general formula C_nH_m and non-combustible mineral substances and moisture.

In presence of a sufficient quantity of air oxygen carbon burns according to the reaction

$$C + O_2 \rightarrow CO_2 + 408.2 \text{ kj (97.65 kcal)} \qquad (44)$$

The equation allows ready calculation of the amount of heat released in the combustion of one kilogram of carbon (or one cubic metre of gas), for gaseous fuel, its heating value*, which is

$$\frac{1000}{12} \cdot 408.2 = 34\,016 \text{ kj (8289 kcal)} \qquad (44)$$

* Other designations are heat value, calorific power, heating capacity.

In case of a lack of oxygen, carbon burns but partly

$$2C + O_2 \rightarrow 2CO \qquad (45)$$

its heating value then being mere 10 250 kj (2452 kcal).

If gases from incomplete combustion of carbon are cooled, soot will be caused to precipitate out according to the reaction

$$2CO \rightleftarrows CO_2 + C \qquad (46)$$

A plume of black smoke that can often be seen above a stack is particles of soot that have separated out of flue gases when the latter have passed from a hot firebox to a relatively cool stack. Black smoke is characteristic of incomplete combustion of fuel.

Hydrogen burns according to the same reaction both in an excess and a lack of oxygen

$$2H_2 + O_2 = 2H_2O \text{ (vapour)} + 438.2 \text{ kj (104. 8 kcal)} \qquad (47)$$

the lack of oxygen resulting in the combustion of a part of hydrogen only.

Hydrocarbons may burn in a number of ways depending on the amount of oxygen available

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad \text{— complete combustion} \qquad (48)$$

$$\left.\begin{aligned} 2CH_4 + 3O_2 &= 2CO + 4H_2O \\ CH_4 + O_2 &= C + 2H_2O \end{aligned}\right\} \text{— incomplete combustion} \qquad (49)$$

A large excess of air is disadvantageous for the combustion of fuel. Besides oxygen (21% O_2), air contains nitrogen (79% N_2). Nitrogen does not take part in combustion, but it heats up and takes with it a part of heat as it is exhausted with the flue gases. The lesser an excess of air, the less is the loss of heat. Particular advantageous is the burning of fuel in pure oxygen or in a mixture of air and oxygen when the amount of nitrogen per unit of oxygen is less than usual.

High moisture of fuel is also disadvantageous, as much heat is consumed in vaporizing water and heating its vapours.

Mineral impurities when burned produce ash which consists of oxides of aluminium, silicon, calcium and other elements. Ash accounts for a relatively small heat consumption, but the greater the quantity of ash, the lesser that of the combustible components. Ash coats particles of fuel

to hinder the access of oxygen to them, and thus slows down combustion. Most undesirable is an easy melting ash which covers fuel particles with a very compact molten film.

Heating values and ash contents of some kinds of fuel are given below.

Fuel	Ash content, % (by mass)	Heating value			
		kj/kg	kcal/kg	kj/m³	kcal/m³
Natural gas	None	—	—	35 600-37 700	8500-9000
Petroleum	0.2-0.3	41 900-46 000	10 000-11 000		
Coal	Up to 10	21 000-29 000	5000-7000	—	—

Use is often made of the concept of a reference fuel having a heating value of 29 260 kj/kg (7000 kcal/kg), which is a convenient means to compare fuels.

For example, the consumption of one kilogram of petroleum having a heating value of 41 800 kj/kg equivalent to that of $\frac{41\,800}{29\,260} = 1.42$ kg of reference fuel.

The temperature that can be obtained by burning a fuel depends on combustion conditions. If all of the heat released by the combustion of a fuel in an enclosed space is consumed for heating flue gases only and is not lost to outside medium, a theoretically maximum temperature of combustion is attained.

Practically, these conditions are very difficult to fulfil as part of heat is lost, and the actual temperature of combustion t_g is less than that theoretical temperature of combustion t_t. The ratio of these two values, pyrometric coefficient, is always less than unity

$$\eta = \frac{t_g}{t_t}$$

Loss of heat is proportional to time, and, therefore, the greater the rate of combustion, the closer η is to unity, its value practically lying between 0.62 and 0.82.

Pyrometric coefficient can be raised by burning fuel with preheated or oxygenated air.

The rate of the chief reaction of combustion of carbon is governed by the surface area value of the fuel, whether the fuel is solid or liquid. The greater the surface area per unity of mass, the readier the access to oxygen and the greater the rate of combustion.

Rapid combustion of a gas requires its good mixing with air, this being attainable if the gases motion is turbulent and vortical.

In metallurgical practice, fuel is often burned in a same furnace space where ore is processed. Efficient use of furnaces requires the volume of the fuel and its consumption to be small. Metallurgy calls for fuels of high heating values and low ash contents since ash may contaminate the products. The best metallurgical fuels are natural fuel oil, coke and high-heat-value coal.

Natural Gas

Natural gas contains from 50 to 97% of methane and other combustible hydrocarbons of the formula C_nH_m, incombustible impurities accounting for not more than 3 to 10% (CO_2, N_2, etc.).

The application of natural gas to nonferrous metallurgy was begun in 1958. Today, nonferrous metallurgy requirements in natural gas are still fairly small, being of the order of 10 milliards of cubic metres per year. A wider use of natural gas in nonferrous metallurgy is barred by the absence of a developed network of gas lines which, however, are being rapidly built.

Petroleum

Petroleum is a mixture of various hydrocarbons. It may serve not only as a fuel, but also as a valuable raw material for the chemical industry. First, petroleum is distilled to recover the low-boiling values such as gasoline, kerosene, ligroin and gasoil. Distillation residue, fuel oil, contains about 85% carbon and 12% hydrogen. Fuel oil is an excellent liquid fuel of a heating value of approximately 41 800 kj/kg

(10 000 kcal/kg) and a valuable raw material for processing into lubricants and tar, and, therefore, the use of fuel oil in many metallurgical processing stages is acceptable only in the expectation of a more extensive application of natural gas to metallurgy.

Rapid combustion of fuel contributes to higher temperatures, a lesser fraction of heat then having time to escape through furnace walls. Combustion of fuel may be speeded up by atomizing it with compressed air and injecting it into furnace space by spray burners. Small droplets of fuel burn while in flight to form a tongue of flame. The amount of primary air which injects the fuel oil is not always sufficient for the latter's complete combustion, and some air, termed secondary air, is supplied additionally by a number of methods.

Coal

Coal is available in many varieties which differ by the content of free carbon, hydrocarbons, ash and resinous substances, the bitumens. When coal is heated without the access of air, hydrocarbons volatilize, but burn in a flame as soon as they come into contact with the air. Coals of high contents of hydrocarbons are referred to long-flame kind (up to 45% of volatile matter), those low in hydrocarbons, to lean ones. Whenever high temperatures are essential, coal, chiefly of the long-flame kind, is burned in pulverized state. To this end coal is crushed and ground to a size of about 0.05 mm, then injected into a furnace by compressed air via special burners, coal particles then burning rapidly in flight, similarly to droplets of fuel oil.

Heating value of pulverized coal should not be less than 25 140 kj/kg (6000 kcal/kg), and the contents of ash and of volatile matter, respectively not more than 15% and not less than 25%.

Coke

Some metallurgical furnaces require solid lump fuel. It should be mechanically strong and porous to allow rapid combustion. Coal is sufficiently strong, but cracks when heated. Besides, it is compact and burns at a slow rate.

Coke is manufactured from special grades of coal that contain bitumens. Coal is crushed to a size of about 5 mm, moistened and charged into chambers of coke ovens. The air-tight chambers are heated on the outside to 900-1000°C. Volatile matter is run off to coolers where valuable chemical products (resins, benzene, toluol, etc.) are condensed, while combustible coke oven gas is drawn out of the cooler.

Due to melting and subsequent solidification of bitumens, coal in the chambers frits into a solid porous mass, the coke. On discharge, coke is quenched, cooled by water, and crushed, the product being solid porous silvery coke lumps of a heating value of about 27 230 kj/kg (6500 kcal/kg).

Coke oven gas, composed of hydrogen (50%), methane (27%) and other hydrocarbons, may serve as a valuable fuel whose heating value is close to 18 800 kj/m^3 (4500 kcal/m^3). It is partly used to heat coke ovens, the balance being employed as fuel for miscellaneous needs.

Calculation of Air Consumption and Amounts of Products of Combustion in Burning of Fuel

The calculation is conducted for 100 kg of coal the composition of which is as follows:

	C	H_2	N_2	O_2	S	Ash	H_2O
% (by mass) . .	74.3	3.5	1.2	1.7	1.8	13.5	4.0
kilomole/100 kg	6.19	1.75	0.04	0.05	0.06	—	0.22

The bottom values have been obtained by dividing the percentage by the atomic or the molecular mass*.

On the basis of the chief reactions of combustion

$$C + O_2 \rightarrow CO_2$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$S + O_2 \rightarrow SO_2$$

we find the required amount of kilomoles of air oxygen and subtract from it the quantity of oxygen contained in the fuel. Air oxygen requirements then will be equal to, kilomole

$$6.19 + \frac{1.75}{2} + 0.06 - 0.05 = 7.08$$

* Atomic mass and molecular mass are new designations, recommended by the International Organization for Standardization, for atomic and molecular weights. The traditional designations "molecular weight" and "atomic weight" fail to reflect accurately the physical sense of these values.

Air is composed of 21% O_2 and 79% N_2 by volume. Molar ratio is expressed by the same digits: 1 kilomole of any gas has a volume of 22.4 m^3. Therefore, the quantity of nitrogen that enters with oxygen is, kilomole

$$7.08 \cdot \frac{79}{21} = 26.65$$

Required quantity of air is

$$7.08 + 26.65 = 33.73 \text{ kilomole}$$

or

$$33.73 \cdot 22.4 \approx 755 \text{ m}^3$$

The amount of combustion gases is determined in accordance with the same reactions, the nitrogen of the fuel being added up with that of the air, and the water resulting from combustion of hydrogen, with that of the fuel.

The combustion gas total is:

	CO_2	H_2O	N_2	SO_2	Total
kilomole/100 kg	6.19	1.75+0.22	0.04+26.65	0.06	34.91
% (by volume)	17.7	5.6	76.5	0.2	100.0

The volume of combustion gases is, m^3

$$34.91 \cdot 22.4 = 782$$

The calculation has been conducted for a theoretical air consumption, whereas a rapid and complete combustion requires an excess of air, designated by the coefficient α.

For example, for $\alpha = 1.5$ the amount of air for the above purposes will be, m^3

$$755 \cdot 1.5 = 1133$$

7. Refractory Materials

Refractories are construction materials that are capable of withstanding without melting temperatures of up to 1600°C. Refractoriness is determined by the character of the initial deformation of a specimen of a standard shape as it is gradually heated.

Besides refractoriness, refractory materials are required to have an adequate spalling resistance, or not to crack when exposed to sharp variations in temperature, and to withstand chemical attack by slag and salt melts. Depending on intended applications of the refractory materials, their density, heat and electric conductivities are considered either.

Raw materials for the manufacture of common refractory products are high-melting oxides and chemical compounds of aluminium and silicon oxides, obtained by burning refractory

clays, whose melting points are as follows: Al_2O_3—2050°C; SiO_2 — 1713°C; MgO — 2800°C; CaO—2570°C and Cr_2O_3— 2275°C.

Refractory bricks and miscellaneous articles are manufactured by mixing the starting oxides with small amounts of binders such as clay or lime and moistening them. Once mixed to a homogeneous state, the mass is moulded into articles which are then slowly dried to avoid cracking. Then the articles are burned in special furnaces by gradually raising the temperature to 1350-1600°C (depending on composition and grade). After a predetermined holding at a prescribed temperature, the items are gradually cooled.

Chemical nature of oxides that makes up the refractory materials varies. Calcium and magnesium oxides are bases, whereas silicon dioxide has acid properties and aluminium oxide is amphoteric, displaying either acid or basic properties depending on the surrounding medium.

Fireclay items are manufactured from a refractory clay whose chief component is kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The clay is burned at 1400°C with the effect that it loses water and turns to fireclay (chamotte) of a chemical formula of $3Al_2O_3 \cdot 3SiO_2$. When mixed with water, fireclay does not become plastic as the case is with clay. Ground fireclay is mixed with water and fresh clay which serves as a binder. The resultant thick mass is thoroughly worked up, then moulded, dried and burned.

Refractoriness of fireclay items is relatively low, being below 1730°C, but they are cheap and, therefore, find a wide application in metallurgy. In chemical properties, fireclay is neutral. The greater the Al_2O_3 content in the fireclay, the higher its refractoriness. To obtain a most refractory high-alumina fireclay, commercial alumina Al_2O_3 is added to the raw mass.

Magnesite items are obtained from natural magnesite which is burned at 1600°C to remove carbon dioxide according to the reaction (15). The binder is also magnesium oxide, but one obtained by burning at 900°C. Processing stages necessary for the manufacture of items are the same: working up, moulding, drying and burning.

Magnesite items withstand temperatures up to 2000°C and possess chemical properties inherent in bases. They

feature a poor spalling resistance (fail rapidly when exposed to sharp variations in temperature) and a relatively high density (3.65 g/cm^3). Chrome-magnesite brick is manufactured from a mixture of burned magnesite and chrome ore.

Dinas items are obtained from pure quartz sand, a minute amount of refractory clay being used as binder. Silica is an acid refractory of a refractoriness close to 1710°C and high spalling resistance.

Review Questions

1. Who was the founder of metallurgy as a science?
Mendeleev, Lavoisier, Lomonosov, Proust.
2. What metals were smelted in Russia prior to the Great October Socialist Revolution?
Co, Cu, W, Al, Mg, Ag, Zn, Ti, Pb.
3. What common properties are characteristic of metals?
Hardness, refractoriness, forgeability, electric conductivity, resilience, heat conductivity, lustre.
4. What metals are rapidly oxidized by air oxygen and what others are not oxidized at all?
Ca, Cu, Fe, Au, K.
5. Name metals that occur naturally in native state and form no sulphide minerals.
Ti, Pb, Au, Cu, Al.
6. What is a measure of the affinity of metals for oxygen and sulphur?
Atomic mass, melting point, density, isobaric potential of formation of oxides (sulphides).
7. Name metals that can be settled out at the cathode by electrolysis of water solutions.
Al, Zn, Ca, Cd, Ag.
8. Name chemical formulae of minerals quartz, galenite, sphalerite, pyrite.
FeS_2, SiO_2, PbS, ZnS.
9. Dressing of 100 tons of lead ore, containing 2% Pb, yielded 4 tons of a 40% Pb concentrate. Determine the percentage of lead recovery to concentrate.
10. What fuels are used in metallurgy?
Peat, petroleum, fuel oil, generator gas, natural gas, coke, coal.
11. What chief substances make up refractory materials?
Al_2O_3, Fe_2O_3, FeO, CaO, MgO, $MgCO_3$, Cr_2O_3.
12. Name acid, basic and neutral refractory materials.
Dinas, magnesite, fireclay (chamotte).

PART I

HEAVY NONFERROUS METALS

CHAPTER 1

GENERAL

8. Use of Heavy Nonferrous Metals and Alloys

Copper, nickel, lead, zinc and tin are termed in the Soviet Union heavy nonferrous metals. This name has originated at the time of industrialization of the USSR in connection with the concept of "heavy industry" and its importance for the national economy. At the same time, the name appropriately distinguishes the heavy metals from equally as important aluminium and other light metals of appreciably lower density.

The conventional boundary between the heavy and the light metals is a density of 5000 kg/m^3. Literature on metallurgy in languages other than the Russian carries no similar terms. However, this rough generalization has proved itself to be a convenient means to group major nonferrous metals whose importance in modern engineering is second to that of iron only.

Iron has long ago become the chief material for structures, machine-building and transport. However, development of new branches of industry and engineering has brought to light some of iron's shortcomings. It goes without saying that all that has been said on the subject refers not to pure iron, but to its industrial alloys, cast irons and steels. While possessing a great variety of valuable properties, common cast and steels, nevertheless, are not sufficiently resistant to corrosion in the air, particularly to that involving attack by water and by solutions of salts and acids. They are low in heat and electrical conductivities and exhibit a high coefficient of friction.

From the beginning of 19th century, heavy nonferrous metals and their alloys found use as substitutes for iron in industrial applications that required particular properties in which cast irons and steels were lacking.

Copper

Copper has high heat and electrical conductivities, in which it is inferior to silver only. Owing to its plasticity, copper can readily be rolled, stamped and drawn. With the advent of electricity, copper became the chief material for conductors, buses, contacts and other electroconductive parts.

High heat conductivity of copper makes it a suitable material for all heat conducting devices, in the first place, heaters and coolers. In chemical industry, copper is used to make coiled pipes for heating or cooling solutions, boiling kettles, conduits and other parts of chemical engineering apparatus.

Even negligible admixtures of other elements greatly reduce electrical conductivity, heat conductivity and corrosion resistance of copper. These properties can be put to effective use only if copper carries not more than 0.05% of impurities.

However, pure copper is too soft for structures, components of machines and apparatus. Its alloys with other metals are much stronger and harder, and many of them surpass copper in still other valuable properties, e.g., in corrosion resistance and antifriction properties.

Alloys of copper with 10 to 40% Zn called brasses, although cheaper than pure copper, can readily be pressure shaped and machined, and are strong, hard and resistant to corrosion. Small admixtures of iron, aluminium and manganese in various combinations make brasses even stronger and harder, whereas admixtures of tin, aluminium, manganese and nickel enhance their antifriction properties. Brasses find extensive application in chemical and general machine-building, shipbuilding and military engineering.

Bronzes were formerly called alloys of copper with 6 to 20% of tin that found extensive use because of their excellent mechanical, antifriction and anticorrosion properties. At a later date, with tin becoming scarce, development

work led to a successful manufacture of alloys similar to bronzes by admixing metals other than tin to copper. Today, a wide use is made of aluminium (5-11% Al), lead (25-33% Pb), silicon (4-5% Si), beryllium (1.8-2.3% Be), cadmium (up to 1% Cd) and other bronzes, along with tin bronzes. All these alloys carry small amounts of secondary alloying components, which enhance the various properties of copper. Each kind of bronzes is valuable within its field of application: aluminium bronzes with additions of lead are suitable for bearings while beryllium bronzes are used in the manufacture of springs.

Brasses and bronzes, similarly to many other alloys, are subdivided into foundry and pressure shaped varieties, suitable either for foundry work or for pressure shaping by rolling, forging, stamping and drawing.

Copper-nickel and copper-nickel-zinc alloys, i.e., cupronickel (5-35% Ni) and German silver (5-30% Ni and 13--45% Zn), are particularly resistant to attack by aggressive media, containing active chemical substances. These alloys are used in the form of strip, sheet and wire to make medical instruments, precision mechanics manufactured items, table covers, home appliances and works of art.

Copper is known from ancient times, and the Bronze Age was a period of swift developing material culture. Later on, bronze was supplanted by the cheaper and the more readily obtainable iron, but as large industrial production developed, consumption of copper began to rise at a fast rate.

Copper was the first among nonferrous metals in world output until 1958 when it was moved to second place by aluminium. Copper is still a scarce metal, and so many substitutes are used. In electrical engineering, copper is more and more being replaced by aluminium, which is less electroconductive, but lighter, an additional advantage being that consumption of aluminium in electrical applications is, by mass, almost half that of copper. In railway transport, copper and bronze are being partly replaced by zinc alloys. In military engineering, cartridges and gun shell cases are made from brass-coated steel instead of bronze. Substitution of copper by other less scarce metals and alloys is an important task of present day engineering.

Nickel

As compared to other heavy nonferrous metals, nickel is stronger, harder, more refractory and more corrosion resistant. Similarly to iron and cobalt, it is ferromagnetic. Pure nickel is plastic and readily workable.

Nickel is relatively costly, and its consumption as a pure metal is low. Nickel is used for plating iron, aluminium, zinc and other metals (nickel-plating) with a view to protecting them against corrosion and for ornamental purposes. Nickel sheets, pipes and wire are used for special components of apparatus and instruments in the chemical industry.

Nickel is also required for the manufacture of alkali iron-nickel and nickel-cadmium storage batteries, which are lighter, more compact and dependable in operation than the lead ones. Nickel catalyzers find their applications in many chemical processes.

More than half of nickel is consumed for the manufacture of nickel-iron alloys. Chromium-nickel, stainless and acid-resistant steels, commonly with up to 8% of nickel and with admixtures of chromium and other metals, are widely used in the chemical industry, machine tool manufacture, building of durable structures, general machinebuilding and military engineering. Strong and wear-resistant nickel cast irons, alloyed with chromium, molybdenum and copper, are necessary for the manufacture of heavy internal combustion engines for locomotives and of special machine tools and dies.

Many nickel alloys are chemically resistant at high temperatures in air atmosphere. Classed with these types are alloys: inconel, nimonik, gastelloy, etc., which can withstand temperatures of up to 600°C. They are used for turbines of jet aircraft, gas turbine power plants and in nuclear reactors.

Nichrome (75-85% Ni, 10-20% Cr, the balance, iron) and other similar thermoelectric nickel alloys are not only refractory, but possess high ohmic resistance and are suitable for wire or strip resistor heaters.

Strongly magnetic alloys of nickel with iron (permalloys) and other similar alloys find extensive application in electrical and radio engineering.

Of alloys of nickel with other nonferrous metals, the most important are copper-nickel alloys that have been discussed previously.

The first metallic nickel was obtained in Sweden by Klaproth in 1751, and its production for marketing began in 1825 only and remained at a low level for a long time. Many valuable properties of nickel were not discovered until the beginning of the 20th century, this explaining why the demand for nickel began to grow rapidly at the turn of the century.

Today, consumption of nickel is under strict control in all industrial countries, and means are devised to minimize its consumption. To this end, an ever greater part of nickel in stainless steels is replaced by chromium, while common steels are clad (plated) with thin coats of stainless steels to serve in applications where solid stainless steel was previously used.

Lead

Lead is known to man from ancient times, since no less than two thousand years B.C., when of particular value were its ready workability and high density. Lead was used to make coins, ornaments, miscellaneous vessels, water pipes, projectiles for slings and catapults. With the invention of powder, lead found use for the manufacture of case-shot, bullets and shot.

Abilities of lead to resist attack by diluted sulphuric, chlorhydric acids and many other chemicals have made the metal in the 19th century the chief material for the then nascent chemical industry. Lead is very amenable to rolling. Sheet (rolled) lead, 2 to 10 mm thick, is suitable for anti-corrosion coating of various apparatus.

Sheaths of electric cables intended for prolonged underground service, in water or moist surroundings are even today made from lead blended with small amounts of other metals to enhance the former's plasticity.

Lead storage batteries are as before necessary to start internal combustion engines, notwithstanding the availability of nickel storage batteries, which are much costlier. About half of all the lead produced is used in the manufacture of electric cables and storage batteries.

In nuclear engineering, lead serves as a shield against γ-rays, which it absorbs better than various other materials.

In military engineering, lead is still needed for the manufacture of shrapnel and cored bullets.

Lead alloys differ from the pure metal either by greater strength and hardness or by antifriction properties, and what is more, most of the alloys are resistant to corrosion.

Alloys featuring low friction, babbitts (so named after their inventor Babbitt) are subdivided into tin and tin-less varieties. The former carry, besides lead, also copper, antimony, cadmium, nickel and tellurium. The latter include sodium, calcium, tellurium and other elements. Babbitts are low-melting, they are melted and cast into bearing shells or applied in a coat of appropriate thickness upon a steel strip.

Printing alloys for casting type contain antimony, tin and copper, in addition to lead. Antimony makes the alloys hard, while tin greatly improves their castability.

Alloys of lead and antimony, hard and corrosion-resistant, find extensive use in chemical engineering.

In soldering alloys, or solders, lead may partly replace the costly and scarce tin.

The demand for lead is much in advance of its output, and a continual search is going on for various substitutes. Electric cables are sheathed, wherever feasible, by plastics instead of lead, and anti-corrosion coats are being manufactured of synthetic organic materials. Lead printing alloys are often replaced by zinc alloys, and it is not inconceivable that they will be manufactured of plastics sometime in the future when latter's castability is adequately improved.

Zinc

Data on the history of zinc metallurgy are most various. Some evidence tends to show that zinc was manufactured in India and China as early as the 5th century, but industrial manufacture of zinc in Europe started as late as the 18th century in England, then in Upper Silesia.

Today more than half of zinc output is consumed for coating iron to protect it against corrosion. A coat of zinc

can be applied to iron either by a high-temperature technique or by electrolysis. An electrolytic coat is thinner, and zinc consumption is more economical. However, simpler equipment makes high-temperatured zinc-coating generally preferable to electroplating. Zinc reliably protects iron against corrosion in the air and in cold water. Zinc-plating is considerably cheaper than tin-plating or nickel-plating.

Another important field of application of zinc is the manufacture of alloys, inclusive of the already mentioned brasses and German silver.

Zinc-based alloys, partly employed instead of bronzes and babbitts in bearings, contain aluminium (8-11%), copper (1-2%) and magnesium (0.03-0.06%). Identical components, but in a different ratio to zinc, are contained in printing alloys, similar in properties to lead-antimony alloys.

In comparison to other nonferrous metals, zinc is less costly, and it is found in sufficiently great amounts in prospected deposits, and so no need ever arose for its substitutes. With the growth in the output of aluminium and further decrease in its cost, it may happen that calorizing, or coating with aluminium, will become more advantageous than zinc plating.

9. Ores of Heavy Nonferrous Metals and Ore Dressing

Characteristics of Heavy Nonferrous Ores

Ores of heavy nonferrous metals are either sulphides or oxides, other varieties being a rare occurrence. Ores with more than $^3/_4$ sulphides are considered sulphide ores, and those with less than $^1/_4$ sulphides, oxide ores. Other kinds of ores are generally termed mixed.

Sulphide ores formed when molten magma solidified, and the process involved crystallization of the melt and condensation of evolving vapours and gases. Sulphide ores are geologically the oldest ones.

Oxide ores are commonly the product of a secondary transformation of sulphide ores, namely oxidation and weathering near the earth's surface under the action of the air and soil water. But some oxide ores may have formed according

to different processes. Oxidation and weathering may cause sulphide minerals gradually to turn to oxides, carbonates, silicates, and other oxygen compounds. Sulphides of copper, nickel, lead, zinc, and their permanent companion iron, frequently occur as solid stony masses which undergo slow geological transformations.

Sulphide ores are either massive or disseminated, characteristic of the latter being impregnation of quartz or other rock with fine sulphide grains. Disseminated ores oxidize more readily than massive ones since their sulphides have large aggregate surface area and are surrounded by looser and more porous rock. Depending on the type of deposits and weathering conditions, sulphide ores change either to oxide or mixed ores.

Characteristic of heavy nonferrous ores is their complex nature, or simultaneous presence of minerals of different metals, e.g., sulphides of copper and nickel (copper-nickel ores), sulphides of lead and zinc (lead-zinc ores). Even more complex ores, e.g., the copper-lead-zinc ores are quite a common occurrence.

Natural sulphides are always accompanied by noble metals. Presence of silver in the form of argentite Ag_2S and native gold is characteristic of copper, lead and zinc ores, whereas platinum and platinum group metals (osmium, ruthenium, rhodium, rhenium, iridium and palladium) are companion metals in copper-nickel ores.

Typical of heavy nonferrous metal ores are associated metals whose percentage is relatively low. There are very few ores of associated metals and then their deposits are rare; this explains why associated metals are obtained as by-products of heavy nonferrous metals manufacture. Some copper ores carry molybdenum; copper-nickel and nickel ores, cobalt; and lead-zinc ores, bismuth and cadmium.

Besides minerals of nonferrous metals, sulphide ores also carry pyrite FeS_2 and, less frequently, pyrrhotite Fe_7S_8. There is particularly much pyrrhotite in copper-nickel ores, its crystals often containing nickel as fine inserts or solid solutions.

Minerals of associated metals are not always separate grains. They are often finely dispersed in minerals of heavy metals or form substitutional solid solutions.

Table 8

Chief Minerals of Heavy Nonferrous Metals

Mineral	Formula	Density, kg/m³ (g/cm³)*	Hardness
	Copper Minerals		
Bornite	Cu_5FeS_4	4900-5200 (4.9-5.2)	3
Chalcocite	Cu_2S	5500-5800 (5.5-5.8)	2.5-3
Covellite	CuS	4600 (4.6)	1.5-2
Chalcopyrite	$CuFeS_2$	4100-4300 (4.1-4.3)	3.5-4
Malachite	$CuCO_3 \cdot Cu(OH)_2$	3700-4100 (3.7-4.1)	3.5-4
Chrysocolla	$CuSiO_3 \cdot 2H_2O$	2000-2200 (2.0-2.2)	2.4
Native copper	Cu	—	—
	Nickel Minerals		
Pentlandite	$(Fe, Ni)_9S_8$	4500-5000 (4.5-5)	3.5-4
Garnierite	$Ni_4[SiO_{10}] \cdot (OH)_4 \cdot 4H_2O$	2300-2800 (2.3-2.8)	2-2.5
Revdinskite	$(Ni, Mg)_6 \cdot [Si_4O_{10}](OH)_8$	2500-3000 (2.5-3)	2-2.5
	Lead Minerals		
Galenite	PbS	7450(7.45)	2.5
Anglesite	$PbSO_4$	6100-6400 (6.1-6.4)	2.5-3
Cerussite	$PbCO_3$	6400-6600 (6.4-6.6)	3-3.5
	Zinc Minerals		
Sphalerite (zinc blende)	ZnS	3900-4200 (3.9-4.2)	3.5
Smithsonite	$ZnCO_3$	3400-3500 (3.4-3.5)	4.5

* The measurements are made in the SI system, while the limits in brackets are in the CGS system.

Sulphur of pyrite and other sulphides is a substantial value, and it is highly desirable to extract it in elemental state, to produce from it sulphuric acid and liquefied sulphurous anhydride or to utilize it one way or another. Regular companions of sulphur, selenium and tellurium, are valuable rare elements of great importance in certain new fields of engineering.

Apart from pyrite and pyrrhotite, ores always carry quartz SiO_2 and various silicates of aluminium, iron, calcium and magnesium. Silicates are salts of silicic acid, which has a tendency for polymerization, i.e., to complication of molecules, this explaining the complex composition of natural silicates. In our short discussion, silicates may be simply considered compounds of oxides: SiO_2, Al_2O_3, FeO, CaO, etc., the bond between them being denoted by a dot, e.g., $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

Oxide ores of heavy nonferrous metals consist chiefly of oxides, carbonates and silicates. They contain the same values, but generally very little sulphur, which is primarily bound into sulphates. Oxide ores occur nearer the surface than the sulphide ones, this explaining why many of them have already been mined. Nickel and copper oxide ores only have retained importance in present-day extractive metallurgy.

Contents of heavy nonferrous metals in sulphide and oxide ores are units and tenths of a per cent, richer ores being very rare. Assay of noble metals ranges from units to tens of grams per ton. That of molybdenum, bismuth, cadmium is in hundredths and less frequently, tenths of a per cent. Sulphur in sulphide ores may be as high as 40% and even 50%.

Chief minerals of heavy nonferrous metals are given in Table 8, while Table 9 lists some ore compositions.

Composition of an ore or concentrate is described by the percentage of elements or simplest oxides, this being the elemental composition. Metallurgical (charge) calculations require the knowledge of mineralogical composition, termed also phase composition. It is expressed in percentage of minerals or chemical compounds. Mineralogical composition is calculated from chemical analysis and mineralogical investigation. Let us consider an example of such a calculation,

Table 9

Examples of Chemical Compositions of Heavy Nonferrous Metal Ores

Ores	Content of components, % (by mass)									
	Cu	Ni	Pb	Zn	Fe	S	SiO_2	Al_2O_3	CaO	MgO
Copper sulphide	1	—	—	—	40	42	10	3	—	—
Copper oxide	2	—	—	—	2	—	75	6	—	—
Copper-lead-zinc sulphide	3	—	6	7	20	30	20	3	—	—
Copper-nickel sulphide	2	3	—	—	45	28	10	9	3	4
Nickel oxide	—	1	—	—	12	—	39	5	—	14

Calculation of Mineralogical Composition of a Copper Ore

Chemical analysis has indicated that the ore contains, %: 5.65 Cu; 20 Fe; 6.2 Zn; 25.9 S; 23.3 SiO_2; 10.2 Al_2O_3; 4.0 CaO; 1.0 BaO; 3.1 CO_2; 0.7 H_2O.

Mineralogical investigations have shown the presence in the ore of chalcopyrite $CuFeS_2$, pyrite FeS_2 and sphalerite ZnS.

The calculation is made on the basis of 100 grams of ore, this being of great convenience as the figures in grams and in per cent are identical.

Minerals that have been identified by mineralogists are composed of copper, iron, zinc and sulfur. Let us express the contents of these elements by the quantities of gram-atoms in 100 grams of ore

$$\frac{5.65}{63.54} = 0.0889 \text{ Cu}; \qquad \frac{20}{55.84} = 0.358 \text{ Fe};$$

$$\frac{6.2}{65.38} = 0.095 \text{ Zn}; \qquad \frac{26}{32.07} = 0.811 \text{ S}$$

1 g-atom of copper gives 1 mole of $CuFeS_2$, therefore, the amount of chalcopyrite in the ore is 0.0889 mole, the chalcopyrite also carrying 0.0889 g-atom Fe, and that of $2 \cdot 0.0889 = 0.1778$ g-atom S.

The content of iron in pyrite is 0.358—0.089 = 0.269 g-atom, and that of pyrite in the ore, 0.269 mole, inclusive of 2·0.269 = 0.538 g-atom S.

The quantity of sulphur in sphalerite is then 0.811—0.538—0.1778 = 0.095 g-atom, and the amount of sphalerite, 0.095 mole.

For a reconversion to per cent by mass, the mole contents of minerals should be multiplied by the corresponding molecular masses.

We thus obtain, %:

$CuFeS_2$	0.0889·183.4=16.3
FeS_2	0.269·120=32.3
ZnS	0.095·97.4=9.2

There are no other data for expressing the mineralogical composition of rock in our example, and so the composition of the ore in terms of component minerals is as follows, %

$CuFeS_2$	16.3	CaO	4.0
FeS_2	32.3	BaO	1.0
ZnS	9.2	CO_2	3.1
SiO_2	23.3	H_2O	0.7
Al_2O_3	10.2		
Total			100.1*

Ore Dressing

Ores of heavy nonferrous metals are beneficiated chiefly by flotation, other techniques being used at a much smaller scale.

Flotation (so termed because the minerals are caused to float, and the rock, to sink) may be briefly described as follows: fine ore pulp is mixed with small amounts of flotation agents agitated with compressed air and vigorously stirred. Once they have adsorbed flotation agents, ore minerals tend to lose their water wettability, with the effect that their grains stick to air bubbles and float to the surface as froth, while rock remains in the pulp. Froth, which carries the ore minerals, is removed and dewatered, the process yielding a concentrate. Rock pulp (tailings) is dumped by pumping and letting it flow along troughs. In districts

* The excess of tenth of a per cent results from rounding out and may be neglected.

where water is scarce, the rock pulp may be first dewatered to reclaim water, then transported to a dump as a thick moist mass.

When appropriate flotation agents are used, it is possible to float as froth all the sulphide minerals, while leaving oxides and pyrite in the tailings pulp, the concentrate thus obtained being known as collective concentrate.

If the collective concentrate is re-floated with different agents, it may become possible to float to the froth successively all the ore minerals one by one and so obtain selective concentrates.

An ore may also be selectively flotated (differential flotation), selective concentrates being produced in succession one after the other from an ore pulp, the residual pulp consisting of tailings only.

It follows from the short description that flotation involves fine grinding of ore and dewatering of flotation products. Discussion of these two processing stages is the subject of the remaining part of the chapter.

It is of interest to compare the cost of different flotation processing stages (in per cent of the total cost) and to ascertain once more that grinding is relatively costly:

Crushing	5.9-18.8
Grinding	26.3-75.3
Flotation	25.1-46.8
Dewatering and drying	10.5-19.4
Other processing stages	3.2-10.5

Crushing and Grinding

Run of mine ore lumps may exceed 1500 mm across, whereas flotation requires commonly particles finer than 0.1 mm. This is why ore is crushed and ground in several stages with the use of different machines. Generally the successive crushing and grinding stages prior to flotation are as follows, mm:

	Feed size, mm	Product size, mm
Crushing:		
coarse	1500-300	300-100
medium	300-100	50-10
fine	50-10	10-2
Grinding	50-10	0.05 and finer

Coarse crushing is effected in jaw and cone crushers. The former (Fig. 6) crush lumps of ore between jaws of hard steel. One of the jaws is fixed, the other is swinging. The surface of jaw plates is undulated and the protrusions of one jaw plate are opposite the hollows of the other. As a shaft with eccentric *3* rotates, connecting rod *4* rises and descends to change the angle between toggles *5*. The movable jaw is

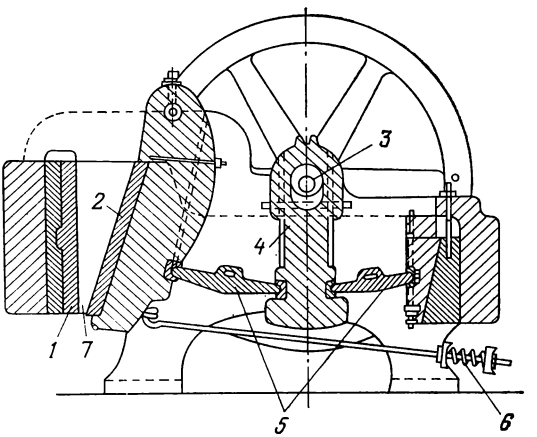


Fig. 6. Jaw crusher

1—fixed jaw; *2*—swinging jaw; *3*—shaft with eccentric; *4*—connecting rod; *5*—toggles; *6*—spring; *7*—outlet

caused to travel toward the fixed one to crush ore lumps, then to back away from it under the load of spring *6*. Crushed ore falls through the feed outlet. The capacity of jaw crushers may be as high as 500 m^3/h.

Gyratory cone crushers of various designs are available in sizes suitable for coarse, medium and fine crushing. Capacity of coarse crushers may be as high as 2300 m^3/h. Crushing surfaces of a unit shown in Fig. 7 are shaped as truncated cones. The smaller of the two cones (head) rolls over the inner surface of the larger one to crush ore lumps.

The top end of the shaft that carries the mobile cone is articulated upon the crusher housing, while the bottom end slides freely in an eccentric sleeve which is rotated by an electric motor via a transmission.

Medium cone crusher (Fig. 8) differs from the preceding one by the absence of a suspended shaft articulation. It has a much flatter mantle or cone than does the above-mentioned

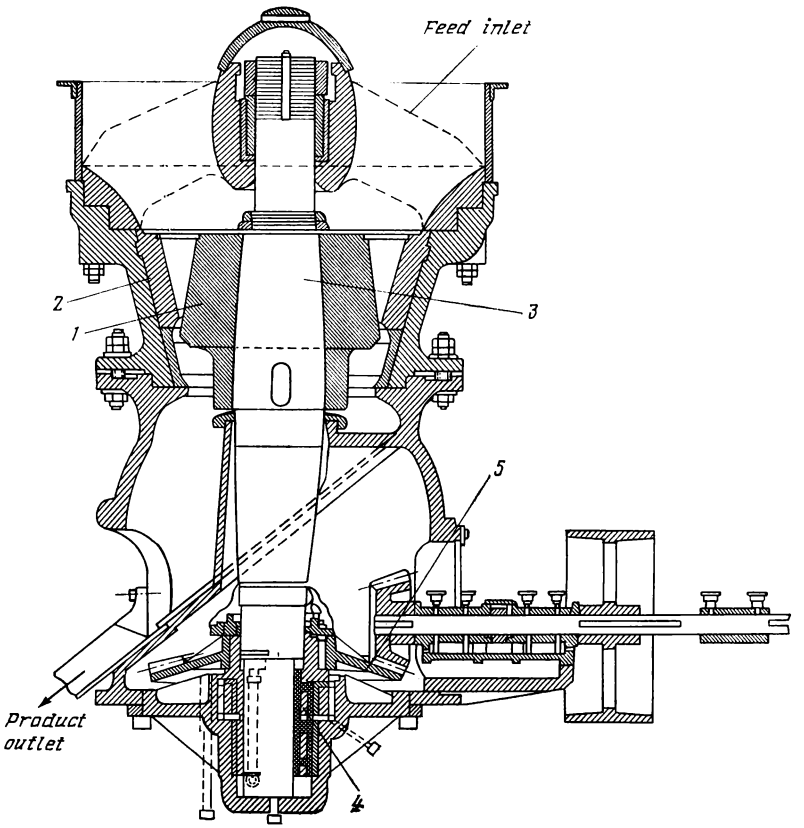


Fig. 7. Coarse crushing gyratory crusher
1—movable crushing head; *2*—concave ring; *3*—shaft; *4*—eccentric sleeve; *5*—drive gear

machine and the crushed product is less coarse and more homogeneous. To prevent damage to the crusher by stray metallic objects, components of the crusher housing have spring-loaded joints.

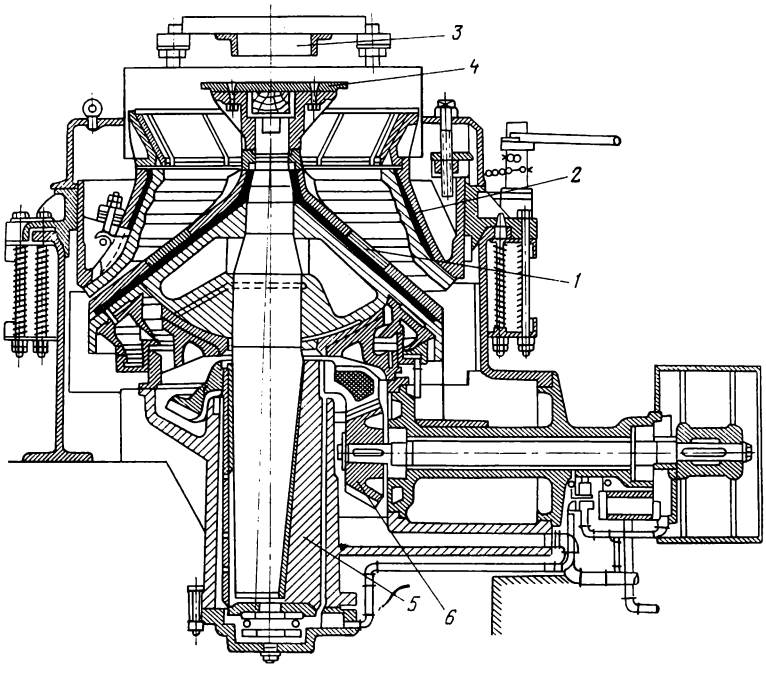


Fig. 8. Medium crushing cone crusher

1—mantle; *2*—fixed bowl; *3*—feed hopper; *4*—feed plate; *5*—eccentric sleeve; *6*—drive gear

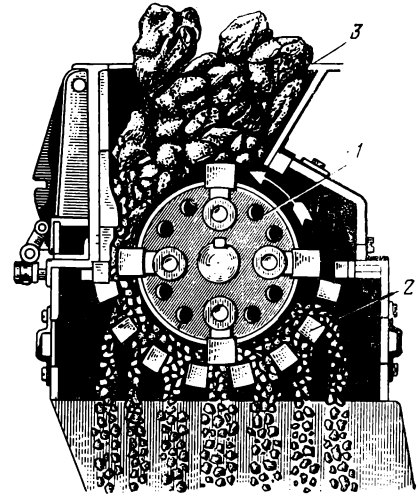


Fig. 9. Hammer crusher

1—rotor with swing hammers; *2*—grid bars; *3*—feed hopper

Coarse, medium and fine crushing of brittle, relatively soft sticky materials is carried out in impact crushers, which are subdivided into hammer mills and disintegrators. The principle of operation of a hammer mill is clear from Fig. 9 and requires no explanation. Its rotor revolves at a speed of 500 to 600 rpm.

Fine grinding of ore lumps less than 50 mm across is done in mills (Fig. 10). The ore is fed into a steel drum loaded

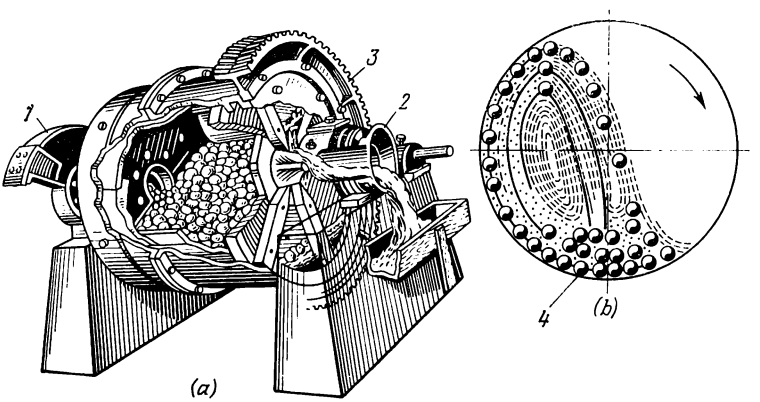


Fig. 10. Ball mill

a—general view; *1*—single-spiral feeder; *2*—outlet hollow trunnion; *3*—drive toothed rim; *4*—balls; *b*—ball path in grinding

with steel rods or balls and rotated about its horizontal axis. Diameters of crushing bodies, rods or balls, range from 20 to 150 mm. The drum rotates at 12 to 40 rpm and the crushing bodies are raised to a certain height then dropped to pulverize the ore.

By the kind of crushing bodies, mills are subdivided into rod, ball and pebble types. In the latter type the crushing bodies are silica pebbles. Of late, extensive use has been made of pebble mills and of autogeneous grinding (in which the crushing bodies are ore lumps themselves) to minimize a high consumption of iron due to intensive abrasive wear of balls or rods and to avoid objectionable contamination of ore by iron.

There are dry and wet (in a pulp) grinding techniques, the latter eliminating evolution of dust and lumping of material.

Mills generally operate continuously. Ore and water are fed through a hollow trunnion at one end of the drum, and a ground material is discharged as pulp overflow through the opposite trunnion.

Pulp consistency is described in terms of solids to liquid ratio (S to L) or percentage of solids by mass. In mill grinding, a pulp may run 40 to 75% of solids.

Required fineness of grinding is obtained by adjusting the feeding rate, or residence time of ore inside the mill.

Ore Sizing

Grindabilities of different minerals may vary in each of the crushing and grinding stages, this being governed by hardness, brittleness, impact strength and shape of lumps of minerals. Products of a crushing stage may be partly finer than a prescribed limit size of products of the downstream crusher and if fed to the latter will increase power consumption and reduce its capacity. Therefore, crusher performance may be vastly improved by sizing the ore after each crushing stage through the agency of screens of various designs, the process being similar to sieving.

A simplest bar screen (Fig. 11) consists of parallel steel bars, or gratings, sloped at 35-40°. Spacing of grates corresponds to sizing limit and is generally not less than 25 mm. Ore slides along the grating and its finer particles fall through the apertures between bars. Bar screens are cheap, but their efficiency is fairly low. They are used upstream and downstream of coarse crushing.

Vibrating screen is a metallic wire cloth fitted upon a frame, vibrated or oscillated by a mechanical drive or solenoids. Different size fractions may be separated by installing a number of screens one below the other. Vibrating screens are used after medium or fine grinding apparatus.

A revolving screen (trommel) has a screen cloth stretched in the form of a cylinder. It rotates about an axis, sloped at a small angle. Ore slides over the inside surface of the screen and gradually moves from the high end to the low

end. Several size fractions may be separated simultaneously by installing concentric screens of different apertures.

Screening is not suitable for fine materials, which tend to lump together and disintegrate readily, and, this is why fine materials are sized in pulps. This type of sizing is ter-

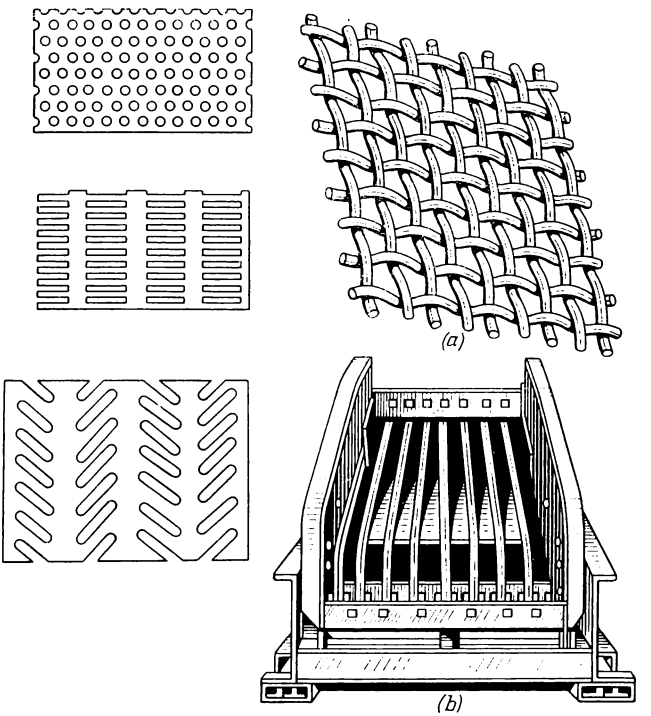


Fig. 11. Screening grates
a—grates for vibrating, rotary and other types of screens; *b*—bar screen

med wet or hydraulic classification, and the apparatus used, classifiers. Hydraulic sizing is based on the fact that the larger (heavier) a particle, the readier it settles in a pulp.

A hydraulic classifier is a vessel fed continuously with ore pulp. During the time the coarser particles (sands) remain in the classifier they settle out while the finer ones float away with the overflowing fluid. The lesser the speed

of travel of the pulp through the classifier and lower its viscosity, the finer the particles in the overflow.

Classifiers of various designs differ in shape of vessel and sand discharge techniques.

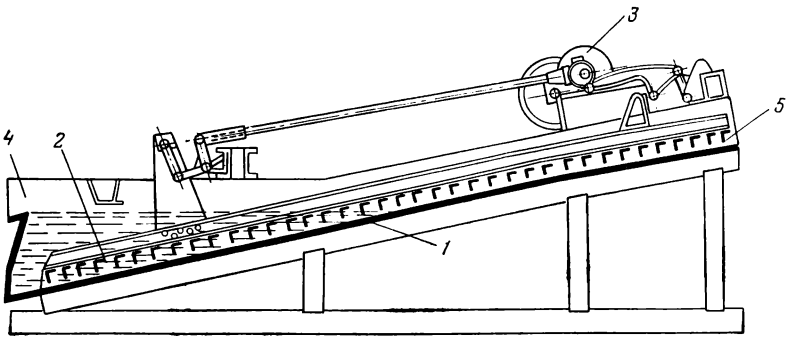


Fig. 12. Rake classifier

1—trough; *2*—rake; *3*—drive for actuating rakes; *4*—overflow lip; *5*—sand discharge

A rake classifier (Fig. 12) is essentially a flat bottomed elongated steel trough. Pulp is supplied via a runner from one of the trough ends and is discharged at the opposite end

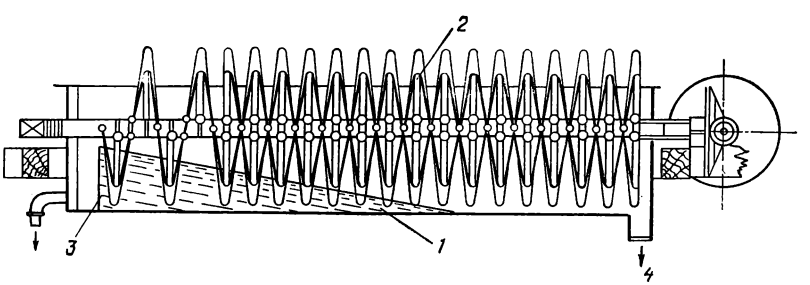


Fig. 13. Spiral classifier

1—trough; *2*—spiral; *3*—overflow lip; *4*—sand discharge

over an overflow lip of adjustable height. Sand, settled out at the bottom of the trough, is gradually transported by a power rake to the raised end and discharged.

A spiral classifier (Fig. 13) differs from the rake one by a semi-circular trough, and the use of a screw conveyor to

remove sand that settles out. The mechanism of the spiral classifier is simpler and more reliable in operation than the rake one.

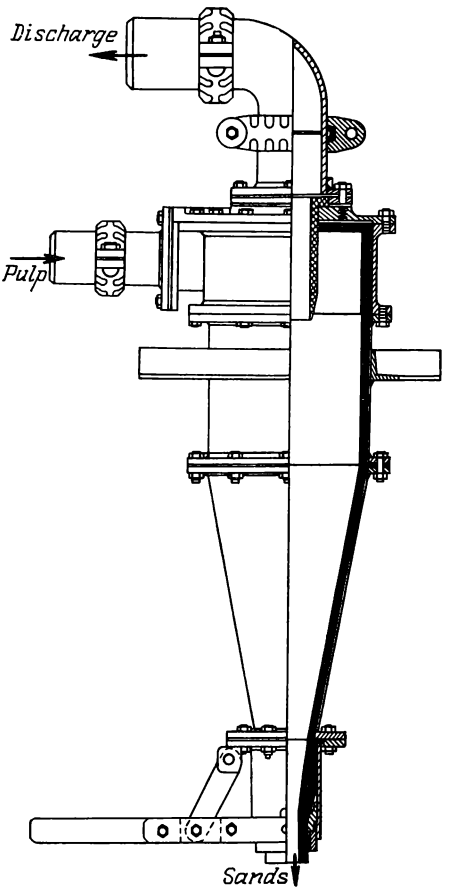


Fig. 14. Hydrocyclone

The often used hydraulic cyclone classifiers are noted for their high capacity (Fig. 14). Large and small particles of pulp are separated in the cyclone by the action of centrifugal

forces. Pulp is fed into the hydraulic cyclone along a tangent to its cross section at a great speed and thus is caused to follow a spiral path inside the cyclone. The larger particles are thrown by the centrifugal force against the walls of the hydraulic cyclone, where they lose speed and settle

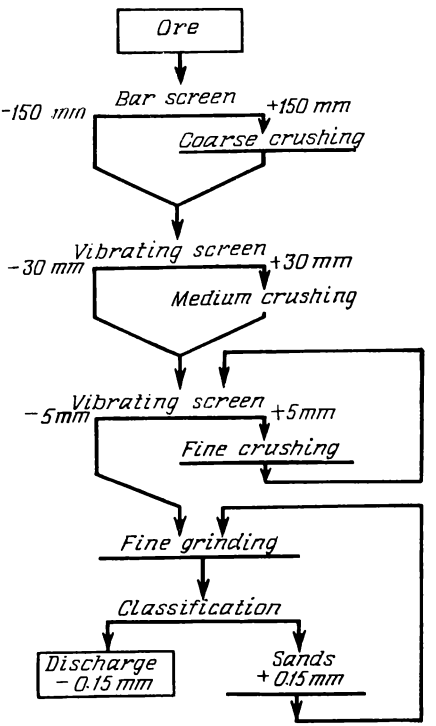


Fig. 15. Flowsheet for crushing, grinding and classification

out in its bottom part, while the finer grains are entrained by the outgoing stream. Hydraulic cyclones are iron castings sometimes lined on the inside with basalt or rubber to protect them against abrasion. Cyclone diameters range from 150 to 500 mm.

Fig. 15 illustrates a typical crushing, grinding and classification flowsheet based on two requirements: not to over-

crush and to discharge a material not larger than a prescribed size. To this end, ore is screened before each crushing stage, and the oversize only is fed to the crusher. The second requirement is met by crushing or grinding in a closed circuit, screen or classifier oversize being returned to the crusher or mill.

Each and every crushing and grinding flowsheet should be judiciously designed and calculated, since these production stages are very costly and over-processing will necessarily bear injury to the economics involved.

Flotation Reagents

As mentioned above, in flotation, grains of heavy minerals, e.g., sulphides, are caused by the flotation reagents to attach themselves to air bubbles and thus float to the surface of the pulp. This type of flotation reagents, collectors, are organic substances with a long hydrocarbon chain, one end of which is polar and presents a chemical affinity for minerals of predetermined composition and structure.

Collectors are commonly salts of xanthogenic acid, the xanthates. For example, potassium ethylxanthate $C_2H_5OCS_2K$ is soluble in water, where it dissociates

$$C_2H_5OCS_2K \rightleftarrows C_2H_5OCS_2^- + K^+ \qquad (50)$$

By its polar end, the xanthate ion attaches itself to sulphides, whereas the non-polar part of its molecule faces the liquid phase.

Non-polar substances are hydrophobic, they make better contact with the air than with water. When a mineral particle, coated by a collector, meets an air bubble it attaches itself to the bubble and is carried by the latter to the surface of the pulp.

Xanthates with different lengths of the hydrocarbon chain, such as ethyl, butyl, amyl and other xanthates, as well as dithiophosphates and other collectors aid to recover to froth the sulphides and to leave in the pulp various oxides, silicates, carbonates and miscellaneous gangue minerals.

Flotation requires but a thin collector film on sulphide particles, so that its consumption is small, commonly not more than hundreds of grams per ton of ore.

Economic consumption of flotation reagents is facilitated by the surface activity of most of them. These substances have the ability to absorb themselves at the solid-liquid interface, their concentration there being much higher than in the body of the pulp. Xanthates react with all the heavy nonferrous metals, and their action upon the latter's sulphides is almost identical. Therefore, in order to separate similar minerals, e.g., sulphides of various metals, the floatability of one of them is suppressed by the use of reagents termed *depressors.*

Depressors are generally soluble non-organic compounds capable of hindering the attachment of collectors to some of the minerals. For example, floatability of pyrite is depressed by the use of lime or soda. Other depressors can suppress the floatability of sphalerite, while leaving unaffected that of copper sulphides and of galenite.

To restore the previously suppressed floatability of a mineral or enhance the attachment of a collector, use is made of *activators,* which are mostly non-organic compounds. For example, the floatability of sphalerite, suppressed by addition to the pulp of sodium cyanide and zinc sulphate, may be activated by copper sulphate (blue vitriol).

Froth-forming agents or frothers are used to make the froth stable and capable of retaining minerals that have floated to the surface. Frothers are various kinds of oils, soaps and resins, in particular, pine oil and creosote. Soaps may be both frothers and collectors in one operation. Frothers, similarly to collectors, are surfactants. They collect at the water-air interface, or on the surfaces of bubbles, and enhance their stability.

Action of flotation reagents is affected by the activity of hydrogen ions in the pulp, on the latter's acidity or alkalinity. Activity of hydrogen ions is controlled by additions of sulphuric acid, lime, soda, soda ash, whichever is required by the acidity or the alkalinity of the medium.

Consumption of various flotation reagents may tentatively be quantified as follows, gram/ton of ore:

Collectors	100-750
Frothers	50-300
Depressors and activators	up to 1300

Agents for controlling pulp acidity are usually added at the end of grinding and are stirred with the pulp by mechanical stirrers in special contact tanks. Sometimes reagents are fed directly to flotation machines.

Flotation Machines and Flowsheets

The operation of a flotation machine consists in a vigorous stirring of the pulp with air bubbles. At the same time, conditions should also be provided in the machine to ensure ready floating of bubbles loaded with mineral particles and to remove mineralized froth from the surface of the pulp.

In present-day production practice, flotation machines operate continuously. By means used to aerate the pulp and to supply the air, the machines are subdivided into mechanical (subaeration), pneumatic and combined types. We shall discuss a mechanical type of machine only (Fig. 16), although today many beneficiation plants tend to prefer pneumatic-and-mechanical machines that incorporate a device for additionally supplying and dispersing air.

Mechanical (subaeration) flotation machines consist of a tank from sheet steel, divided into a number of cells by transversal partitions. Pulp is fed via box *1* along a pipe *2* to the first cell where it is vigorously agitated by impeller *3* (stirrer) covered with disk *4* at the top. The impeller is a paddled wheel from hard steel which revolves at a speed of 275 to 600 rpm and sucks in air from pipe *5* via part *6*. The pulp, mixed with small air bubbles, rises to a free settling zone above grid *8*. From the first cell, the pulp flows to an intermediate box over a weir *9* and successively passes through all the machine cells. A tailings pulp is continuously discharged from the last cell.

The froth product that floats in the cells is driven into a launder by paddles of froth separator *7*. If a re-flotation (cleaning) is necessary the froth product is directed via launder *10* and pipes *11* to the flotation machine cells specially intended for the purpose.

Sometimes products of the initial flotation are ground additionally to break up mineral intergrowths and to allow their separation. Multi-stage flotation alternating with additional grinding often ensures better beneficiation.

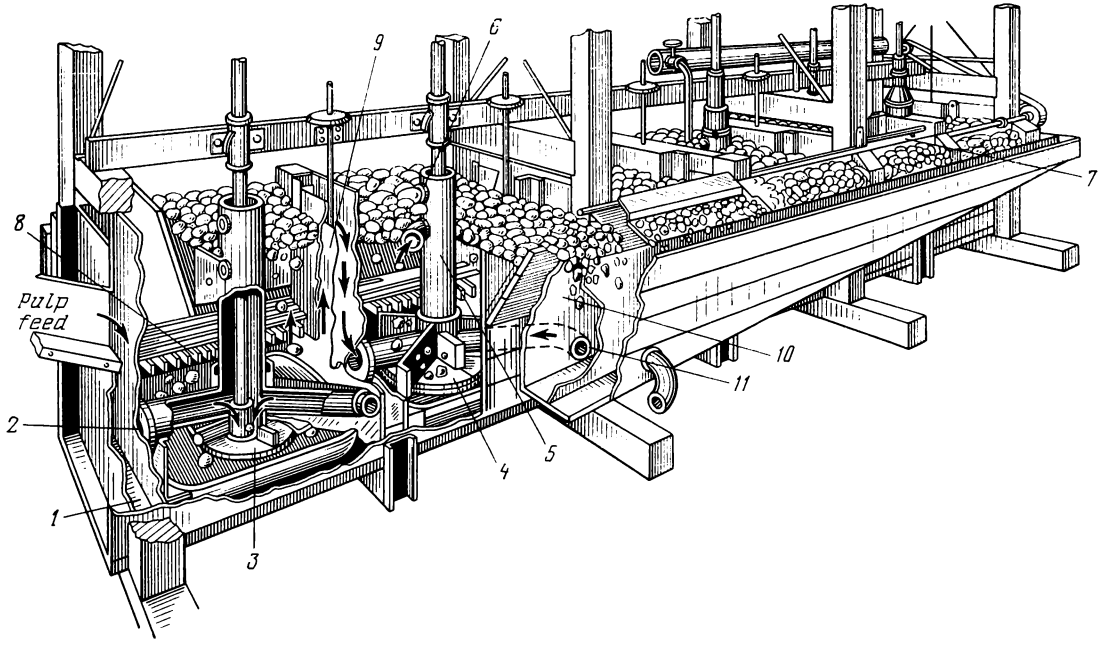


Fig. 16. Mechanical (subaeration) flotation machine

1—box; *2*—pipe; *3*—impeller; *4*—disk; *5*—pipe; *6*—port; *7*—froth separator; *8*—grid; *9*—wier; *10*—launder; *11*—pipes

Dewatering of Ore Dressing Products

Concentrates and tailings that result from beneficiation treatments are pulps with a liquid to solids ratio (L to S) not less 4 or 5 units and sometimes even still more diluted.

Dewatering is carried out successively by three methods: settling (thickening), filtration and drying. Thickening is a cheapest method, but it may decrease the liquid content in a pulp down to 40-50% only. After filtration, the moist residue (cake) may carry as low as 10% of moisture. Cake moisture is affected by the properties of solid particles and their size. The most complete dewatering is attained by drying, but it involves the highest costs and requires fuel.

To thicken a pulp, it is settled in thickeners (Fig. 17). The clarified liquid is termed the overflow, and the deposit, the thickened product or underflow.

Large solid particles settle out of the pulp faster than fine ones. To accelerate settling of fine particles, use is made of additives, flocculators and coagulators, e.g., lime and synthetic organic substances, in particular, polyacrylamide, which cause the particles to agglutinate through cohesion.

Thickeners are cylindrical tanks from wood or reinforced concrete up to 100 m in diameter, provided at the centre with an inlet well which is continuously fed with starting pulp to fill the tank to the level of an overflow launder run around the tank. A clarified overflow runs off continuously into the launder.

Solid particles settle upon the conical bottom of the thickener. At the latter's centre there is a flanged discharge cone with gates and graduated nozzles. Next, the underflow finds its way through pipes to an intermediate tank whence a pump feeds it to the prescribed destination. Deposited material is swept from the edges to the centre by a device consisting of a spider that carries obliquely fitted paddle-shaped rakes. Rotation of the spider's shaft at one revolution every 2 to 8 minutes does not interfere with settling, but is sufficient for the rakes to push the deposited material towards the central discharge cone. In larger thickeners, move than 15 m in dia., the central shaft is often replaced by a stationary column, and the spider, by a truss, which

rides about the column on a carriage that rolls upon the edge of the thickener.

Capacity of thickeners is measured by the surface area of the bottom required to settle out to underflow 1 ton of solids per day (sq. metre per ton-day). This value varies over a wide range, depending on properties of pulp. For

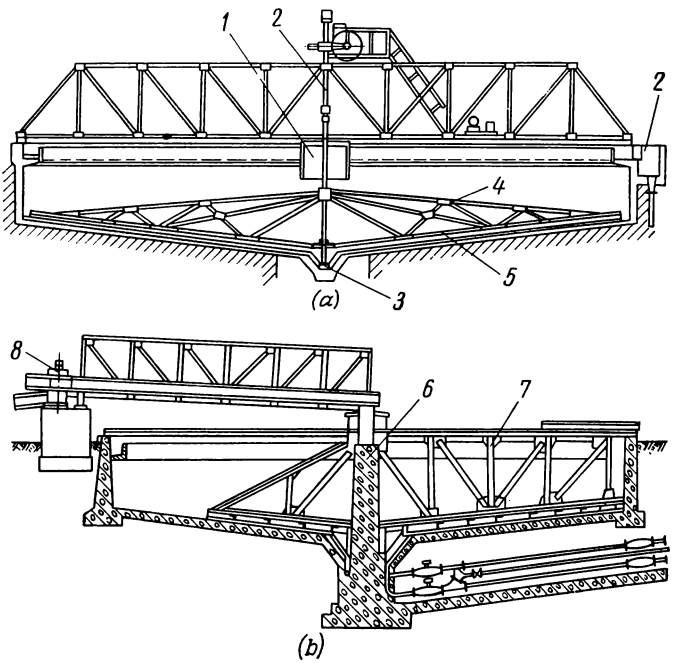


Fig. 17. Thickeners

a—with central shaft; *b*—with rim drive; *1*—central well; *2*—launder for overflow; *3*—bottom discharge well; *4*—truss; *5*—rakes; *6*—column; *7*—rake-carrying truss; *8*—truss-driving carriage

instance, when a pulp of flotation concentrate is thickened from 10 to 60% solids in the underflow, the capacity is 1.2 to 1.7 m^2/ton·day.

Filtration of pulps is based on forcing a liquid through a porous partition that does not pass solids. Filtration materials are cotton and woollen cloths and fabrics from glass and synthetic fibres.

The rate of filtration and the filter capacity related to it depend on the difference in pressures and loss of pressure in the pores of the deposit and the cloth. Filtration slows

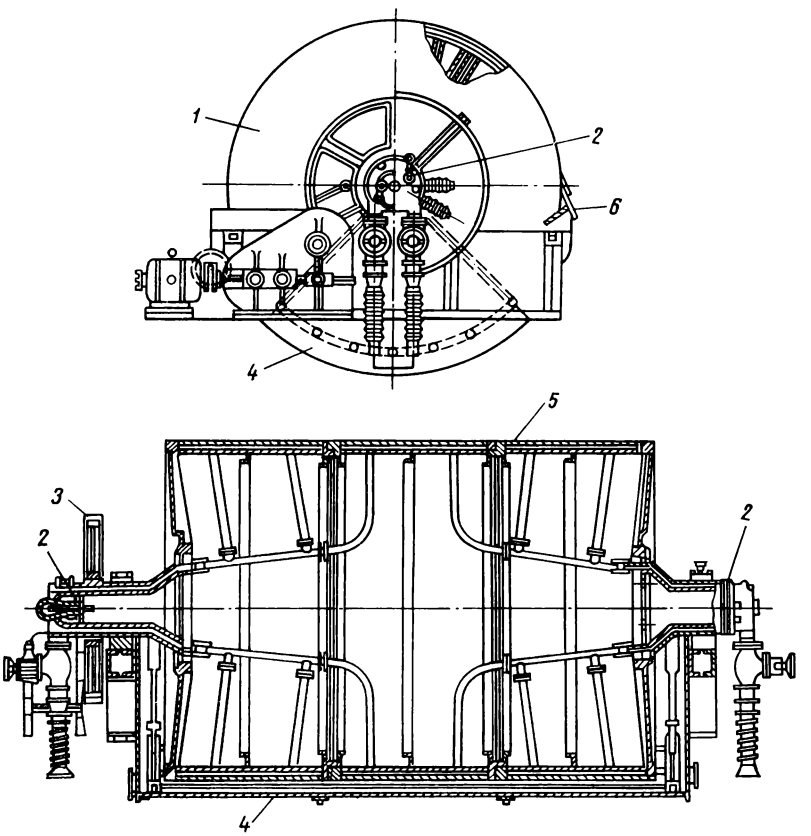


Fig. 18. Drum-type vacuum-filter

1—drum; *2*—distributing slide valve hub; *3*—drive; *4*—trough with pulp; *5*—perforated shell jacketed by filtration cloth; *6*—chute for removing cake

down as the thickness of the deposited cake increases and the cloth pores become plugged by particles of the deposit.

Industrial filters are subdivided into vacuum-filters, in which the difference in pressures results from a vacuum in

the filtrate collector, and filter-presses that operate by the application of a pressure upon the pulp. The present chapter deals with the most common types of vacuum-filters only.

A drum vacuum-filter (Fig. 18) is a horizontal hollow perforated cylinder that is rotative in trunnions and wrapped in a cloth jacket secured by spirally wound wire. Internally the drum is divided into a number of sector-shaped chambers, connected by pipes to a distributing slide valve that branches the chambers, as the drum rotates, alternately to a vacuum line and to a compressed air line.

The bottom-one-third or one-fourth of the drum dips into a trough filled with pulp. The drum revolves at a speed of 0.13 to 2 rpm. The liquid of the pulp seeps through the pores of the cloth, a cake 6 to 15 mm thick building up on the latter's surface. Air is sucked through the cake for sometime to remove the remaining water. If washing is necessary, the cake is sprinkled with water from sprayers. During the last quarter of a revolution the sector-shaped chamber carrying the cake is connected by the slide valve to a compressed air line which blows off the cake upon an inclined chute. All these operations are repeated with every revolution of the drum.

Filter capacity is measured by the mass of dry cake obtained from 1 m^2 of cloth surface area per hour. In the flotation concentrate filtration practice it lies between 0.15 and 0.7 $t/m^2 \cdot h$, depending on pulp properties, chiefly, on the size of solid particles and the liquid-to-solids ratio. Residual moisture content of cake is governed by the same factors.

Rotary disk vacuum-filter (Fig. 19) is in principle of operation similar to drum filters. Filtration cloth is secured to sectors that make up the disks. The surface of a wooden or metallic sector is provided with grooves connected at its summit to a metallic drainage pipe, and through it, to a slide valve. Cake is removed separately from each disk. For same overall dimensions, a disk filter has a greater filtering cloth surface area and a greater capacity than the drum filter.

Tailings are sometimes not dewatered at all, but dumped directly to a natural body of water or artificial ponds. The general practice is to thicken the tailings and pump them

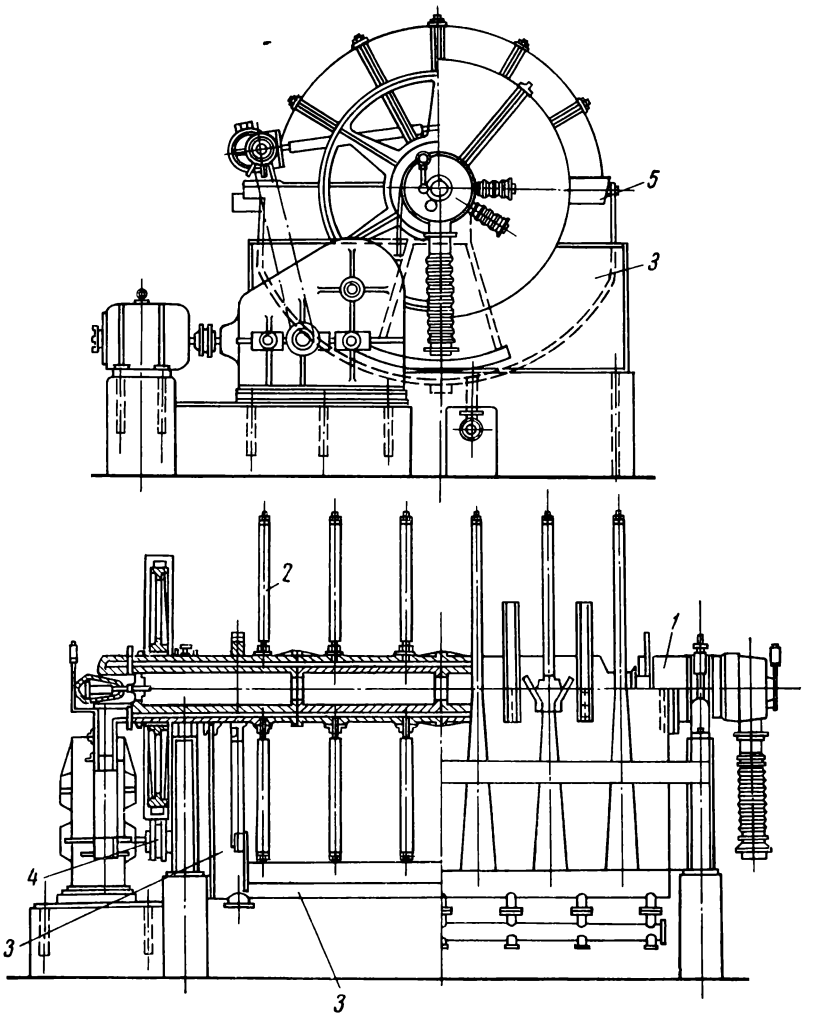


Fig. 19. Disk-type vacuum-filter

1—shaft; *2*—disks assembled of sectors and jacketed with filtration cloth; *3*—trough with pulp; *4*—drive; *5*—chutes for removing cake

to a dump as a thick mass and to recirculate the overflow. The former technique is today inadmissible because of a world-wide anti-pollution campaign. Waste water from beneficiation plants carries flotation reagents and other biologically hazardous soluble substances, and their dumping to rivers, seas and lakes is out of question. Plant operators are trying hard to improve processing flowsheets with a view to increasing recirculation of water and to dump it in least possible quantities. The recirculatory water system should be provided with suitable purification means to avoid inadmissible raise in concentration of soluble substances. Tailings should be properly treated and their dumps should be located, as far as feasible, at adequate distances from bodies of water. The sulphides being dumped carry many bacteria whose activity contributes to the oxidation of iron and sulphur by atmospheric oxygen, dissolved in water, with formation of soluble iron, copper and other sulphates (see Para. 19).

In drying, moisture from a concentrate is removed by the vaporization of water, the rate of vaporization being proportional to a difference in vapour pressure above the material being dried and the gaseous medium that surrounds it. Pressure of water vapours above a material increases with the drying temperature, whereas it is the lower in a surrounding gas, the faster the latter moves to carry away the vapours out of the drier. It should be taken into account that an increase in the speed of gas flow does not accelerate drying ad infinitum, since the transfer of water vapours from the surface of a material to the gases is limited by the rate of diffusion. A fact not to overlook is that too rapid a gas flow may cause excessive dust formation. The layer of a material being dried should be as thin as possible and well stirred.

Dryers are available in a variety of designs, the most common being a rotary cylindrical drier (Fig. 20). This type of drier is essentially a cylinder from sheet steel, 5 to 30 m in length and 0.9 to 3.0 m in diameter, inclined at 3 to 5 degrees to the horizontal. By its two smooth rims, the pipe rests upon rollers whose races are secured to a foundation. A toothed rim engages a driving gear of a gearbox, which is actuated by an electric motor, to rotate the drier at 1.5 to

2 rpm. Internally the driers are provided with radial or any other type of shelves (sometimes chains or a screw conveyor) which cause the material to roll over as the drier rotates and prevent its sticking to the walls. Materials to be dried are charged continuously at the raised end of the drier by

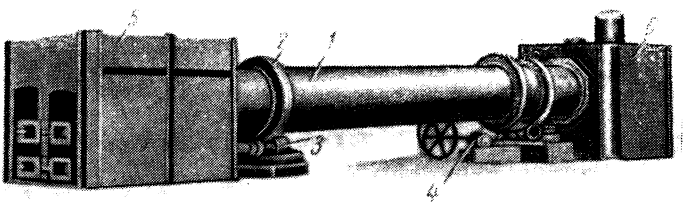


Fig. 20. Drier

1—cylinder; *2*—supporting rim; *3*—roller; *4*—drive; *5*—firebox and discharge of dry material; *6*—charging of wet material

a mechanized feeder and roll from shelf to shelf toward its discharge end. Hot gases (750 to 1000°C) from combustion of a fuel are caused to travel concurrently or in countercurrent, which is an infrequent practice, with the material to heat and dry it.

Other types of driers are used rather as an exception. One of these is described in Para. 9.

Review Questions

1. Name metals that:
(a) are most electroconductive;
(b) are used for the manufacture of storage batteries;
(c) enter the composition of antifriction (bearing) alloys;
(d) are part of bronzes, brasses and type metal.

2. What elements are associated with, nickel, lead, zinc in copper ores?

Cd, Co, Pt, Bi, Au, Ag, S, Si, Fe.

3. What techniques are mostly used to enrich ores of heavy metals?

Gravity separation, magnetic separation, flotation, beneficiation in heavy media.

4. What substances serve as collectors, frothers, depressors, activators, media control reagents in flotation?

Sulphuric acid, pine oil, xanthates, alkalis, creosote, lime, cyanides, copper sulphate (blue vitriol), zinc sulphate (white vitriol).

CHAPTER 12

METALLURGY OF COPPER

10. Chemical Properties of Copper

Copper is a chemical element number 29 of D. I. Mendeleev's periodic table. It has two isotopes with mass numbers of 63 and 65 and an average atomic mass of 63.54. At metallurgical processing temperatures the pressure of vapours of copper, its oxides and sulphides is so small that they may be considered practically non-volatile.

Similarly to its neighbours in the group, alkali metals, copper is univalent, but it features also a stable valency of two with the participation of one *d*-electron.

Salts of univalent copper in water solutions are rapidly oxidized by air oxygen or decompose to divalente and metallic copper

$$2Cu^{+} \rightleftarrows Cu^{2+} + Cu; \quad K = \frac{[Cu^{2+}]}{[Cu^{+}]^2} = 1.6 \cdot 10^6 \qquad (51)$$

In solid state and in melts, the compounds of univalent copper are stable.

Chemical activity of copper is rather small. This follows from values of its electrode potentials as seen from Table 3

$$Cu^{2+} + \bar{e} = Cu^{+}; \quad E^0 = 0.15 \text{ V} \qquad (52)$$

$$Cu^{+} + \bar{e} = Cu; \quad E^0 = 0.52 \text{ V} \qquad (53)$$

Copper does not displace hydrogen from sulphuric and hydrochloric acids and goes into solution in them in presence of an oxidizer only.

In the air at temperatures below 400°C metallic copper slowly oxidizes to CuO, whereas at higher temperatures it forms a scale consisting of CuO, Cu_2O and $CuCO_3 \cdot Cu(OH)_2$.

At temperatures above 800°C, CuO decomposes in the air to cuprous oxide and oxygen

$$2CuO \rightarrow Cu_2O + 1/2O_2 \qquad (54)$$

Cu_2O melts at 1230°C.

Both oxides, CuO and Cu_2O, are readily reduced to metal by carbon monoxide and hydrogen at temperature as low as 450°C. CuO dissolves completely in sulphuric acid, and Cu_2O, with the separation of metallic copper

$$Cu_2O + 2H^+ = Cu^{2+} + Cu \qquad (55)$$

Sulphides of copper CuS and Cu_2S are in many respects similar to oxides. At temperature above 450°C CuS decomposes in a neutral atmosphere to lower sulphide and sulphur

$$4CuS \rightarrow 2Cu_2S + S_2$$

Therefore, at high temperatures Cu_2S only is present in metallurgical melts. Its melting point is 1127°C.

When heated in the air, both sulphides oxidize to CuO and Cu_2O, often through an intermediate stage of formation of $CuSO_4$ and basic salts, $nCuSO_4 \cdot mCu(OH)_2$.

Copper sulphate $CuSO_4$ is readily soluble in water and crystallizes from it as beautiful blue crystals of chemical composition $CuSO_4 \cdot 5H_2O$ (blue vitriol). At pH of about 5.5, diluted solutions of sulphate hydrolize to yield a deposit of basic salts. Characteristic of decomposition of $CuSO_4$ in heating is the formation, first, of basic sulphates, then of oxides CuO and Cu_2O (see reaction 54).

Industrially, copper sulphate (blue vitriol) is used as a pickling agent in dyeing and painting, in the dressing of leather and grain storage. In agriculture it finds its application as a pesticide and a basic material for the preparation of toxic chemicals. Blue vitriol is also used in the manufacture of artificial silk.

By location in the periodic table, close to copper are metals of the same subgroup, gold and silver. They do not oxidize in the air and occur naturally chiefly in native state. Silver is also frequently found as argentite Ag_2S and cerargyrite AgCl. Silver is always univalent, and gold, di- and trivalent. Molten copper, gold and silver are readily soluble in one another.

11. Copper Ores and Their Concentration

Commonly, the content of copper in ores ranges from 0.7 to 2%, richer ores being a rare occurrence. Chief copper ores

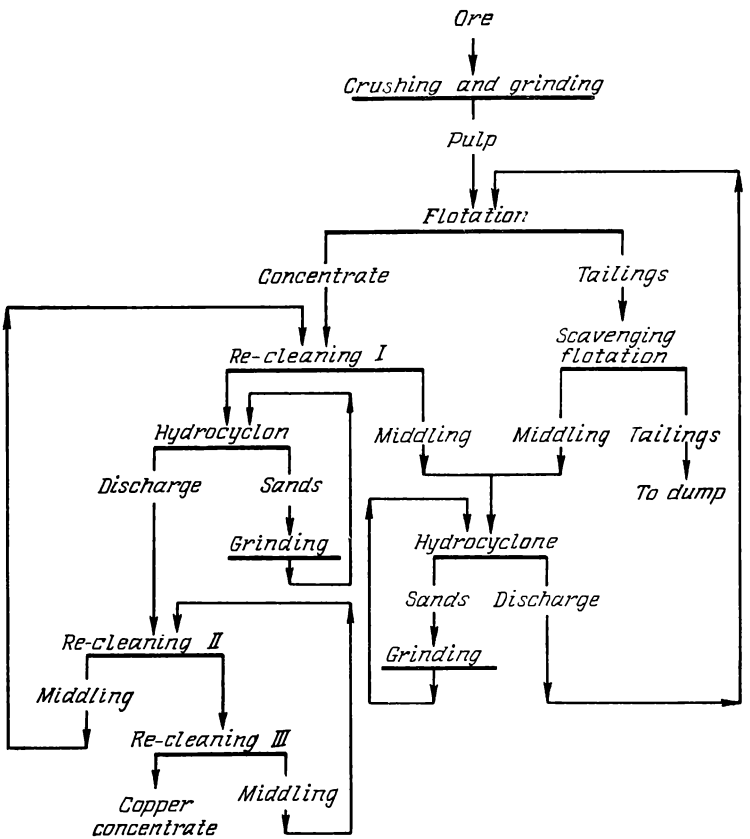


Fig. 21. Typical flowsheet illustrating concentration of phenocryst copper ores

are sulphide phenocrysts, whereas available amounts of solid pyritic, mixed and oxide ores are relatively small.

Sulphide ores are concentrated by flotation, the concentrates containing up to 55% Cu (generally, however, 11 to

35% Cu). The recovery of copper from the concentrates amounts to 80-95%.

A flowsheet for concentrating copper phenocryst ores is given in Fig. 21. It should be noted that basic flotation is carried out after a relatively coarse grinding (to about 0.5 mm). This allows to recover a maximum amount of copper to a primary lean concentrate, which is retreated after an additional grinding to crush growths of copper sulphide with pyrite and quartz.

Pyrite is depressed by lime or soda. Collectors are xanthates or aerofloat (from 35 to 100 grams per ton of ore), and the frother, pine oil (25 to 50 grams per ton).

Flotation of pyritic ores (copper pyrites) requires a fine grinding, sometimes down to 0.044 mm because of an intimate intergrowth of copper and iron sulphides.

Effective flotation of oxide ores is possible only after copper minerals, malachite and azurite, are individuated by sulphidizing with the aid of additions to the pulp of sodium sulphide. Grains of minerals coated with a film of CuS conduct themselves similarly to sulphides.

Chrysocolla neither lends itself to sulphidizing nor can it be recovered by flotation. Also not amenable to flotation is copper bound chemically or by sorption to alumosilicates and hydrated iron oxides.

There is very little oxide copper ores that can readily be concentrated by flotation at a recovery of 75 to 85%. Flotation of difficult-to-treat ores, which yield a recovery of mere 20-30% Cu, is not economically attractive.

Copper concentrates may also be obtained from complex ores by flotation techniques discussed below. Illustrative chemical compositions of different types of concentrates are given below.

Starting ore	Content in concentrate, %						
	Cu	Zn	S	Fe	SiO_2	Al_2O_3	CaO
Copper pyrites	11-20	4-7	35-43	32-37	3-5	3-7	0.5-2
Copper-zinc	11-15	2-4	30-35	25-30	3-5	3-7	0.5-2
Phenocryst	20-25	—	30	25-27	5-10	5-8	0.5-2
Porphyry or sandstone	28-35	—	15-20	16-20	20-29	5-8	1-2

Copper concentrates are all fine powders composed of particles smaller in size than 100 micrometres* and sometimes even finer than 40 micrometres (0.04-0.1 mm).

Concentrating plants produce concentrates with 8 to 12% moisture content after dewatering. Only if distant transportation is involved, are the concentrates dried down to natural hygroscopicity, which is 4 to 6%.

12. Smelting of Copper

Smelting of Copper from Sulphide Concentrates and Ores

In contemporary practice, not all of sulphide ores are treated by flotation. Some of them, those richer and containing negligible amounts of associated metals, are directly smelted to better advantage.

Mineral composition is not affected in concentrating, there being quantitative differences only between an ore and a concentrate from it. Therefore, processing of ores and of concentrates is based on the same physical-and-chemical basis.

When a sulphide ore or its concentrate is smelted, the melt divides into two liquid layers, an alloy of sulphides and an alloy of oxides. Separation into layers is due to a difference in densities and a small mutual solubility of molten sulphides and oxides. The sulphide alloy is termed matte, and the oxide alloy, slag. Slag floats above matte as the density of the latter is about 5, and that of slag, about 3.

Even before melting, as iron and copper minerals are being heated, they substantially change their composition by decomposing to lower sulphides and sulphur vapours

$$2FeS_2 \rightarrow 2FeS + S_2 \quad (56)$$

$$4CuS \rightarrow 2Cu_2S + S_2 \quad (57)$$

$$4CuFeS_2 \rightarrow 2Cu_2S + 4FeS + S_2 \quad (58)$$

$$2Cu_5FeS_4 \rightarrow 5Cu_2S + 2FeS + {}^1/_2S_2 \quad (59)$$

* According to the SI system of units, fractional or multiple units should not be given proper names. Thus, the designation micron (μ), or 10^{-6} m, should be dropped, and the designation micrometre (μm) only should be used.

Lower iron and copper sulphides are stable at higher temperatures, and, therefore, matte is always an alloy of Cu_2S and FeS irrespective of the mineralogical composition of the raw charge. Ready flow of reactions (56) and (57) can be seen from Fig. 5.

Gangue (SiO_2, CaO, Al_2O_3) is transferred in smelting to slag which can readily be separated from the matte and dumped. Therefore, even a plain smelting of an ore or concentrate results in a concentration of copper in a matte.

In order to transfer to slag a part of iron as well, the latter's sulphide should be converted to ferrous oxide by the action of air oxygen

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 \qquad (60)$$

But this is accompanied by a similar oxidation of Cu_2S

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \qquad (61)$$

Practically, however, sulphur of FeS alone is oxidized. The cuprous oxide is re-sulphidized by residual iron sulphide

$$Cu_2O + FeS \rightarrow Cu_2S + FeO \qquad (62)$$

This reaction is considered a basic one in pyrometallurgy of copper. It allows to separate copper and iron, distributing them between molten matte and slag.

As mentioned, in smelting the oxides of copper and of iron will be transferred to slag, and sulphides, to matte. Let us write the activities of the former inside round brackets, and those of the latter, inside square brackets. The equilibrium constant for reaction (62)* will then be

$$K_{62} = \frac{a\,[Cu_2S] \cdot a\,(FeO)}{a\,[FeS] \cdot a\,(Cu_2O)}$$

To calculate K_{62} first determine the change in the isobaric potential of the reaction at smelting temperature in smelting, at, say, 1227°C (1500°K)

$$\Delta Z_{62} = \Delta Z_{Cu_2S} + \Delta Z_{FeO} - \Delta Z_{FeS} - \Delta Z_{Cu_2O}$$

Having made use of diagrams in Figs 3 and 5, we find

$$\Delta Z_{62} \approx -25 \text{ kcal/mole}$$

* In melts, concentrations and activities may be expressed in molar fractions, or the number of gram-moles of a substance dissolved in one gram-mole of the sum of all the components.

From physical chemistry we know that

$$\log K = -\frac{\Delta Z}{RT} = \frac{25\,000}{4.57 \cdot 1500} = 3.65^* \qquad (63)$$

Having assumed activities of iron sulphide and of ferrous oxide respectively in the matte and in slag to be equal, this being very close to their actual values, and having taken a [Cu_2S] to be 0.5, we obtain a very small value for $a(Cu_2O)$, which approximates its equilibrium concentration

$$a\,(Cu_2O) \approx (Cu_2O) = \frac{a\,[Cu_2S]}{K_{62}} \simeq 5 \cdot 10^{-5}$$

The greater the quantity of iron transferred from a sulphide to oxide, the lesser is the amount of FeS remaining in the matte, with resultant increase of copper content in the latter. The degree of desulphurization, which quantifies the oxidation of sulphur, is measured by the ratio of the amount of oxidized sulphur (by mass) to its initial content in the raw materials. The higher the degree of desulphurization, the richer in copper is the resultant matte.

Sulphur can be partly oxidized prior to smelting by means of roasting (which is sometimes used to treat raw materials high in sulphur). If all the sulphur associated with iron is oxidized in roasting or smelting, all of the iron will be transferred to the slag. The matte obtained will be close in composition to pure lower copper sulphide (79.9% Cu). This matte is known as white matte because of a characteristic colour of its fracture.

Copper is obtained from molten white matte by blowing the latter with air. The lower copper sulphide oxidizes in the process to cuprous oxide (62), which, as soon as formed, reacts with the remaining sulphide

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2 \qquad (64)$$

Direct smelting of ore or concentrate to white matte is disadvantageous as an increased copper content in the matte is paralleled by that of mechanical losses of copper in slag because of poor settling of fine droplets of matte. It is good practice to obtain first a relatively lean matte, and correspondingly, a slag low in copper, and to remove the remai-

* Coefficient 4.57 results from the multiplication of R = = 1.987 cal/degree-mole by the modulus for conversion of natural logarithm to a decimal one (m = 2.3026).

ning iron by processing in a converter, which is a metallurgical apparatus for blowing molten matte with air.

At the beginning of blowing, iron sulphide is oxidized (see reaction 60). The resultant ferrous oxide is slagged by

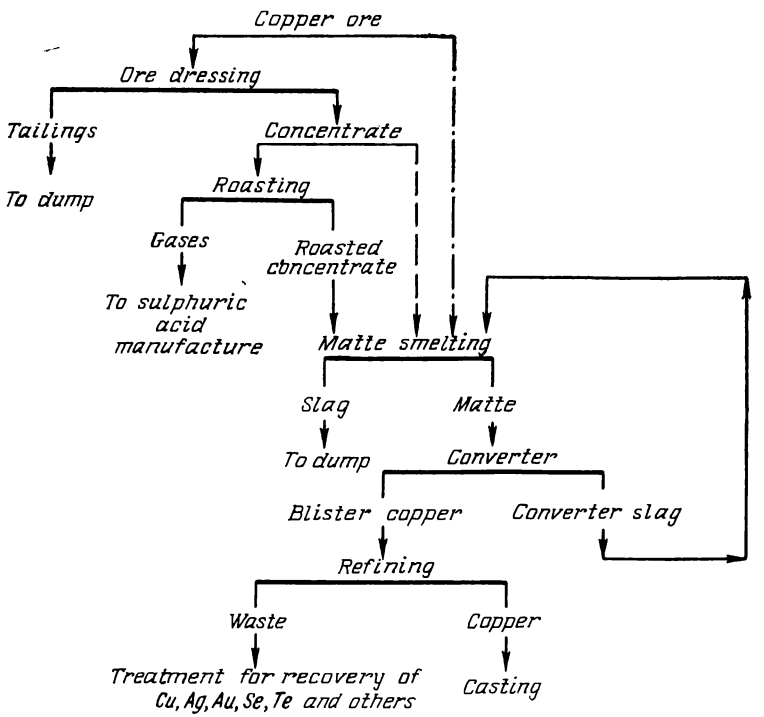


Fig. 22. General flowsheet for smelting of copper
–.–.–.– direct smelting of ore; — — — — — — — smelting of non-roasted (raw) concentrate

quartz which is charged into the converter

$$2FeO + SiO_2 = Fe_2SiO_4 \qquad (65)$$

After white matte is obtained, all of the slag is poured out of the converter and re-treated since it contains much copper. The white matte is further blown with air to blister copper which is then treated to remove impurities, first in refining, then by electrolysis.

Mixed ores contain less sulphur than sulphide ores, and, therefore, they can be processed by the same techniques but with lesser desulphuration. Oxidized ores can be smelted in combination with sulphide ones. Therefore, the matte smelting is suitable for any type of raw materials, provided the latter contains an amount of sulphur sufficient to form a matte.

A general flowsheet of pyrometallurgy of copper is presented in Fig. 22. It shows that copper ores are either concentrated or directly smelted to matte (dash line). The obtained concentrate may be directly smelted (dotted line) or roasted to remove some sulphur. Preliminary roasting allows the use of sulphur for the manufacture of sulphuric acid and contributes to the smelting of richer mattes.

Matte, irrespective of the way it was obtained, is blown through in a converter. Converter slag is high in copper and so is not dumped, but re-smelted with ore or processed separately.

In smelting of an ore or concentrate, noble metals (gold and silver) pass into the matte, and from it, to the blister copper. In the refining of blister copper by electrolysis, noble metals and part of selenium and tellurium are recovered as by-products, which are then processed to pure metals.

Pyrometallurgy is the chief technique for production of blister copper. In the paragraphs that follow it is discussed in detail in accordance with the flowsheet of Fig. 22.

Production of Copper by Hydrometallurgy

Lean oxide and mixed copper ores, difficult of dressing, are processed by hydrometallurgical techniques. Copper is leached out of these ores by solutions of sulphuric acid or ammonia salts, as described in Para. 19.

13. Copper Smelting Mattes and Slags

Mattes and slags are intermediate products of pyrometallurgical manufacture of copper, their properties greatly affecting the performance of manufacturing techniques.

Mattes

As a complement to initial idea of mattes as alloys of Cu_2S and FeS, it should be noted that in practically all the mattes the aggregate content of the above sulphides is but rarely higher than 80-90%, the balance being sulphides of zinc, lead, nickel and oxides of iron, silicon, aluminium, calcium which are slag components that are partly soluble in matte.

Iron oxides are more soluble than others in mattes. Noble metals are readily soluble in molten mattes, and gold and silver pass to matte in smelting.

Maximum possible content of copper in matte is 79.9% (pure Cu_2S). There is no point in obtaining mattes with less than 10% of copper, since their processing is difficult and costly. Mattes generally carry 20 to 40% Cu.

Iron sulphide runs 36.4% S, and lower copper sulphide, 20% S. A study of plant mattes has shown them to contain an average of 24 to 26% S. This allowed Prof. V. Mostovich to derive a rule according to which in metallurgical calculations the content of sulphur in any copper matte may be assumed equal to 25%.

In his investigation of mattes, V. Mostovich established that they contain oxygen in the form of ferrites, chemical compounds of the type $MeO \cdot Fe_2O_3$, e.g., $FeO \cdot Fe_2O_3 = Fe_3O_4$. A matte may contain up to 7% of oxygen. The higher the oxygen content, the leaner is a matte in copper.

Melting point and density of a matte are its major properties that depend on its composition. Richer mattes are of both higher density and melting point as compared to leaner ones. Plant mattes melt at temperatures between 900 and 1150°C, their densities ranging from 4600 to 5200 kg/m^3 (4.6 to 5.2 g/cm^3).

Slags

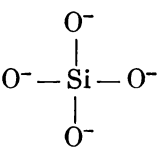
Copper smelting slags are similar in composition and properties to other nonferrous slags. Smelting of nonferrous metals from raw materials always calls for their separation from iron by transferring the latter to slag, and, therefore, a high FeO content is characteristic of most of the nonferrous slags.

Metallurgical slags are silicate alloys, or salts of silicic acid in which hydrogen is replaced by various cations. In ferrous metallurgy, the cations are chiefly calcium and magnesium, and in nonferrous metallurgy, divalent iron and calcium.

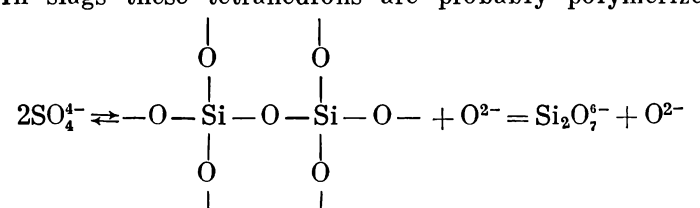
Not long ago it was considered that silicates in slags separate to oxides, and slags were treated as plain oxide alloys. These ideas underlay the outdated *molecular theory* of slags, which is still to be taken into account, since it is the basis on which rests a host of published experimental data on melting, viscosity and surface tension of slags. Actually, silicates dissociate similarly to salts, e.g.

$$Fe_2SiO_4 \rightleftarrows 2Fe^{2+} + SiO_4^{4-}$$

The simplest anion of orthosilicic acid SiO_4^{4-} may be pictured as a tetrahedron with an atom of silicon at the centre



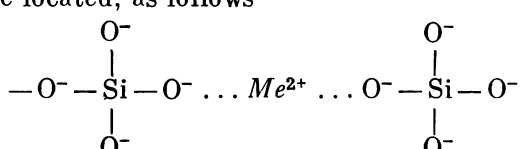
In slags these tetrahedrons are probably polymerized:



In general terms, if a similar construction is continued in the direction of free bonds, we obtain a chain, a closed ring or a network describable in terms of empiric formula

$$Si_nO_{3n+1}^{(2n+2)-}$$

Cations of iron (divalent), calcium, magnesium and other metals are located, as follows



whereas metals capable of forming amphoteric oxides, aluminium and iron (trivalent), may additionally replace atoms of silicon at coordination number of four. Solid silicates produce lattices with sites of ions of silicon, oxygen and metals. In a melt near the melting point this order is retained to a lesser or a greater degree, but it is gradually lost as the melt overheats, the dissociation, by contrast, is increasing.

Molten slags possess ionic electroconductivity, and when subjected to electrolysis, metals are deposited at the cathode, and oxygen, at the anode.

Slag is only a waste or a by-product, but the economic performance of metallurgical smelting greatly depends on its fall (or yield) and properties. Major properties of slags, viscosity and density, affect copper losses, whereas their melting points govern the temperatures of smelting and the attendant consumptions of fuel and refractories.

Losses of metals with slags are generally classified as chemical, physical and mechanical.

Chemical losses have their origin in incompletion of the chief smelting reaction with the effect that some amount of oxide of the metal being smelted remains dissolved in slag. In particular, copper is lost in slag as Cu_2O because the latter is incompletely sulphidized by iron sulphide. .Calculations and practice tend to show that chemical losses of copper are relatively small (63, 64).

Physical losses are related to a solution of metals or matte in slag or formation of colloidal solutions. These losses tend to increase with the temperature and the concentration of Fe (trivalent).

Mechanical losses may be caused by poor settling of fine droplets of metal (or matte) due to a small difference in densities, too short settling time or high viscosity of slag. Losses of this kind account for a sizable portion of the total.

Slags are classed with glassy substances which have no clear-cut melting point. As temperature rises, solid slag gradually softens and becomes less and less viscous. Fusibility of a slag is generally described by a temperature of adequate fluidity for a given type of smelting technique. Too high an overheating causes excessive consumption of fuel and is detrimental to the service life of furnace lining.

Insufficiently heated slags, on the other hand, are viscous, and their settling from mattes is poor.

Viscosity of slags is measured in poises*, its desirable values in copper smelting being below 1 $N \cdot s/m^2$ (10 poises), the corresponding melt temperature ranging from 1100 to 1250°C.

Mattes are much less viscous than slags. Besides, matte droplets settle in molten slag, and, therefore, slag viscosity has a major effect upon settling efficiency.

Copper smelting slags are in many respects similar to slags of nickel and lead manufactures: chief components are the same (SiO_2, FeO, CaO). The aggregate of these components approximates 90%. Besides, slags contain up to 15% Al_2O_3 and in particular instances up to 25% Fe_3O_4 (converter slags), and some amounts of oxides of magnesium, barium, sodium and other metals.

Fusibility of slags is related to the mass ratio of their chief constituents. Fusibility has been thoroughly studied and the results of investigations published as diagrams or tables which allow a ready choice of a slag composition.

An essential point in the choice of a slag is the mass ratio of oxides SiO_2, FeO and CaO in the raw materials. Copper ores and concentrates generally carry more FeO and less CaO than required for obtaining an adequate slag. Therefore, smelting involves the addition of fluxes which are gangue rich in calcium oxide and silica and are commonly quartz and limestone.

In order to minimize the fall of slag, fluxes should be added in least possible quantities. A mixture of ores or concentrates with fluxes, or charge, is composed in accordance with a calculation based on chemical compositions of ore and fluxes.

It is good practice to use gold-bearing ores as fluxes, since noble metals are extracted to matte parallel with copper.

When choosing a slag, its density should be adjusted to a lowest possible value to improve separation from matte. Slags with a high content of a relatively heavy oxide FeO (density of 5500 kg/m^3) are less desirable than those rich in

* In the SI system of units, viscosity is measured not in poises, but in Newtons per second per square metre ($N \cdot s/m^2$); 1 poise = $= 0.1\ N \cdot s/m^2$.

lime (density of CaO is 3400 kg/m^3) or in silica (density of SiO_2 is 2700 kg/m^3).

A major property of a slag is its surface tension at the interface with matte (or metal) and gases. If poorly wettable by slag, fine droplets of a metal or matte may be floated by gas bubbles similarly to the flotation of heavy mineral particles to the surface of the pulp by air bubbles.

A proof of the ionic character of electric conductivity of molten slags is their electrolysis, metal being deposited at the cathode, and oxygen, at the anode.

Slags may also contain salts of aluminic acid, aluminates of the type $Me(AlO_2)_x$, and salts of ferric acid, ferrites of the type $Me(FeO_2)_y$.

14. Roasting of Copper Concentrates

Depending on sulphur content, concentrates are smelted either without roasting (raw charge) or after roasting. Preliminary roasting is one more processing stage. However, its cost pays back in terms of a greater recovery of sulphur.

The purpose of roasting is to oxidize sulphides of the concentrate so as to reduce the sulphur content of the charge and allow the smelting of a sufficiently rich matte. Once heated to ignition point, sulphides burn with a generation of heat, the general form of the reaction for a divalent metal being

$$2MeS + 3O_2 \rightarrow 2MeO + 2SO_2 - \Delta H \qquad (66)$$

where ΔH is the heat of the reaction, j or cal.

The equilibrium of similar reactions is shifted to the right, since their equilibrium constants, expressed in a general form below, are very great

$$K_{66} = \frac{p^2_{SO_2}}{p^3_{O_2}}$$

Pressures of vapours of MeS and MeO are not part of the equation for K_{66}, but are included in its value, as their vapour pressures are constant so long as the temperature remains unchanged.

Thermodynamic calculations show a possibility of oxidation of sulphides even at room temperatures (298°K). An example is sulphides which smell of sulphurous gas when

finely ground, but this, of course, has no practical application, since the rate of the reaction is infinitely small. The above example serves a useful purpose in that the comparison of ΔZ or K values for the two reactions cannot be the basis for judging on the preferable flow of one of these, since it always depends on the rate of the reactions.

As oxygen interacts with a sulphide, a more or less solid and strong film of oxides is formed on the latter's surface (Fig. 23). As roasting progresses, the film grows thicker, its permeability to gases decreases, the oxidation of the sulphide slows down and may even stop altogether. It is self-evident that this concerns less the finer particles than the larger ones which may carry a thicker film of oxides. Preliminary grinding of a material speeds up its roasting, since the surface area per unit of mass of sulphides increases.

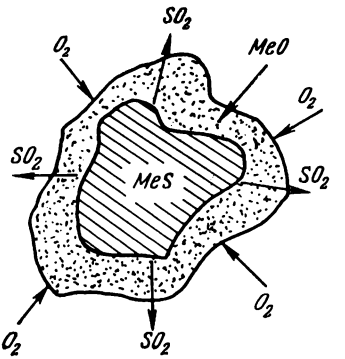


Fig. 23. Oxidation of sulphide mineral grain particle

Oxidation of sulphides requires a continuous exchange of matter between the solid and the gas phases, i.e., penetration of oxygen to the sulphide and removal of the reaction product, sulphurous gas. All these processes are effected through diffusion of gases via pores and cracks in the oxide films, the diffusion increasing with the temperature, but there being a limit to the latter because of a risk of fusion of the grains.

The rate of diffusion is also governed by the difference of partial pressures of oxygen and of sulphurous gas at the interface with the oxide film (see Fig. 23). The less the content of SO_2 and the higher that of O_2 in gases surrounding sulphide particles, the more intensive is the diffusion exchange of matter between the solid and the gas phases, and consequently, the higher the roasting rate. Therefore, particles falling or suspended in a gas are roasted faster than those lying on a hearth. Oxidation on a hearth may be somewhat speeded up by stirring.

A lesser fraction of heat released in the oxidation of a sulphide is consumed for raising the temperature of a burning grain, the greater part being dissipated in the surrounding medium. In roasting of falling or suspended particles the input of heat per unit time is substantially greater, whereas the rate of exchange with the surrounding medium remains practically unchanged. Therefore, heat accumulates in the burning particles, raising their temperature, and consequently, that of roasting.

Ignition temperatures differ with the various sulphide minerals. Besides, it is the higher, the coarser the grains.

Average size of flotation copper concentrate particles is about 0.07 mm. Their chief combustible constituent is pyrite, its content being 40 to 50%. In the combustion of 1 kg of pyrite to Fe_2O_3 the heat release amounts to 6749.4 kj (1607.0 kcal) which is more than enough to sustain a spontaneous oxidation of the concentrate. The effect of all this is that roasters require no consumption of extraneous fuel, roasting thus being a relatively inexpensive processing technique.

Copper concentrates are roasted either in multi-hearth roasters with mechanical rabbling or in fluid-bed roasters. A multi-hearth roaster (Fig. 24) is a vertical cylinder from plate steel. It is lined on the inside with fireclay (chamotte) brick. Along its height, the roaster is divided into separate compartments by dome-shaped hearths from fireclay brick or refractory concrete. The hearths are numbered from the top to the bottom, the topmost hearth being the zero or the drying hearth.

A steel vertical shaft is intended to stir the material being roasted. It carries arms from heat-resisting cast iron, two above each hearth, fitted with oblique paddle-like rabbles. The bottom end of the shaft rests upon a step bearing and is fitted with a gear drive actuated from an electric motor. Rotating at a speed of 2 to 3 rpm, the shaft not only rabbles the material on the hearths, but also moves it from the centre toward the periphery or from the periphery toward the centre of a hearth. Opposite direction of motion of the charge on even and odd number hearths is obtained by setting the rabbles at different angles to arm axis.

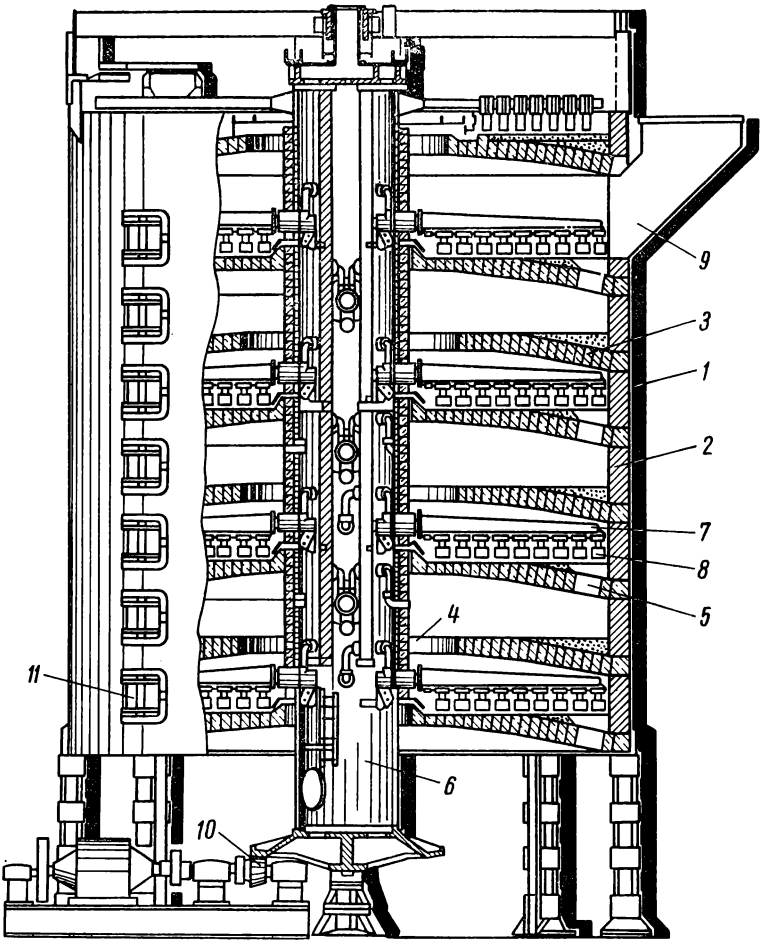


Fig. 24. Multi-hearth roaster

1—shell; *2*—refractory lining; *3*—hearths; *4*—central annular opening; *5*—peripheral discharge hole; *6*—shaft; *7*—arm; *8*—rabble; *9*—flue; *10*—drive gear; *11*—working ports

Concentrates are roasted together with fluxes required in the subsequent smelting, this being a major advantage as the charge is thoroughly mixed in the roaster and heated by the heat of combustion of sulphides.

The charge is continuously supplied by a mechanized feeder at the centre of the dry hearth and gradually rabbled onto the first hearth. Its motion on the first hearth is directed to an annular opening around the shaft through which it falls to the second hearth, etc., the charge thus passing through all of the roaster hearths. Air for the oxidation of sulphides is sucked in through ports. The gases move from the bottom to the top, countercurrent to the charge, following the same zig-zag path and are exhausted from the first hearth via gas flues.

When starting up the roaster, the middle and the bottom roaster hearths are heated by burners or temporary fireboxes whose operation is discontinued once the concentrate has ignited.

The maximum temperature of roasting of 850°C develops at the middle hearths.

Arms are cooled by air to prolong their service life. Each arm consists of two concentric pipes, the outside pipe being plugged and fitted with rabbles. Cooling air is supplied through the inside pipe and exhausted into the hollow shaft or the roaster.

Roasters generally used to process copper concentrates are designed with ten working hearths and one drying hearth. The outside diameter of such a roaster is 6.5 m, and height, 9.6 m.

As it moves from top downwards from hearth to hearth, the concentrate gradually heats until the sulphides ignite or decompose to lower sulphides and sulphur according to reactions (56-59), and resultant FeS and Cu_2S oxidize in accordance with reactions (60, 61).

Vapours of sulphur burn to SO_2

$$S_2 + 2O_2 \rightarrow 2SO_2 \qquad (67)$$

and partly to SO_3

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad (68)$$

Catalysts of reaction (68) are oxides of metals, in particular, Fe_2O_3.

Complex sulphides may also oxidize directly, without dissociating

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \quad (69)$$

$$2CuFeS_2 + 6O_2 \rightarrow Cu_2O + Fe_2O_3 + 4SO_2 \quad (70)$$

$$2Cu_5FeS_4 + 12O_2 \rightarrow 5Cu_2O + Fe_2O_3 + 8SO_2 \quad (71)$$

Arsenopyrite dissociates similarly to other higher sulphides

$$FeAsS \rightarrow FeS + As \quad (72)$$

Arsenic is readily volatile, it vaporizes and oxidizes in gases to As_2O_3

$$4As + 3O_2 \rightarrow As_4O_6 \quad (73)$$

In case of a great excess of air, the oxidation proceeds further

$$As_2O_3 + O_2 \rightarrow As_2O_5 \quad (74)$$

Direct oxidation of arsenopyrite is also possible and gives the same effect

$$2FeAsS + 5O_2 \rightarrow Fe_2O_3 + As_2O_3 + 2SO_2 \quad (75)$$

As_2O_3 vapour pressure attains 98.1 kN/m² (1 atm*) at as low a temperature as 460°C, and, therefore, arsenic is readily removed from the roaster with the gases. By contrast, the pressure of As_2O_5 vapours is relatively low. Besides, this acid oxide interacts with basic oxides FeO or CaO to form arsenates, e.g., $Fe_3(AsO_4)_2$. The greater the excess of air in roasting, the greater the fraction of arsenic is bound into arsenates and remains in the calcine.

Sulphurous gas is partly oxidized by excess oxygen to SO_3 which may combine with metallic oxides to give sulphates, e.g., lead and calcium sulphates, that are stable at higher temperatures.

Solid constituents of roasted concentrate interact among themselves: acid oxides SiO_2, Al_2O_3, Fe_2O_3 interact with

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* One technical atmosphere (1 atm) is equal to 1 kgf/cm², i.e., 1 atm = 1 kgf/cm². Having expressed on the right-hand side of the above equation the kilogram-force in Newtons, and the centimetre in metres, we obtain: 1 atm = $9.81 \cdot 10^4$ N/m². Therefore, 1 atm = $= 9.81 \cdot 10^4$ N/m² = 9.81 kN/m².

basic oxides FeO, CaO, Cu_2O, etc., to form compounds of the type of salts such as silicates, aluminates and ferrites.

Decomposition of carbonates is facilitated by the presence of SiO_2 and SO_3, which form more stable salts, and, therefore,

$$CaCO_3 + SO_3 \rightarrow CaSO_4 + CO_2 \quad (76)$$

$$2CaCO_3 + SiO_2 \rightarrow Ca_2SiO_4 + 2CO_2 \quad (77)$$

$$2MgCO_3 + SiO_2 \rightarrow Mg_2SiO_4 + 2CO_2 \quad (78)$$

Reactions among solid substances often fail to go to completion because of deterioration of mutual contacts, this explaining why roasted concentrates often carry substantial amounts of both starting materials and products of the above reactions.

Temperature in roasters is governed by the concentrate's sulphur content, the feed rate and the amount of air entering the roaster. Capacity of roasters increases with the temperature. The choice of the temperature conditions depends on the composition of materials being roasted, chiefly on the presence of easy melting components. Copper concentrates may frit due to the formation of alloys FeS—Cu_2S whose minimum melting points range from 960 to 1000°C. The temperature at individual points, e.g., near a rabble in motion, may often greatly exceed the average temperature inside the body of the charge. Taking all these factors into account, the copper concentrate roasting temperature is generally maintained not above 850°C.

The quantity of air allowed to enter the roaster is limited by the necessity to obtain gases with not less than 4% SO_2 in order to make them suitable for sulphuric acid production. Besides, increased air consumption results in excessive dust formation, the outgoing gases entraining as much as 10-12% of material being roasted.

Multi-hearth roasters require much floorspace and are rather inefficient. One such roaster of the above size handles up to 250 t of charge per 24 hours, sulphur being burned out from 24-25 to 10-12% and roaster gases containing up to 7% SO_2. It should be stressed that even such a relatively low performance is attained only through a systematic strict control over chemical composition and size content of the

charge, chemical composition of calcine, temperature of gases on the hearths and amount of air admitted to the roasters. Roasting conditions, temperature and draft inside the roaster, are supervised and controlled with the aid of recording instruments.

In recent years there is a marked trend in copper metallurgy to introduce more efficient fluid-bed roasting techniques which differ from the above not only by greater capacity but also by a possibility to obtain gases with higher SO_2 content.

A fluid-bed roaster is shaped as a cylinder or a prism. Its roof and walls are held in place by a steel shell, lined on the inside with refractory concrete. The hearth is a steel plate also protected against the action of high temperature by a layer of heat-resisting concrete.

The hearth plate carries holes for air nozzles that are located in a staggered pattern. Air supply boxes (see Fig. 74) are set tight against the underside of the hearth plate.

When fine materials are charged on the above hearth and air is blown through the nozzles via the air boxes, the charge will be brought to a condition known as fluidized state. Air jets will cause the particles to rise to a certain height, then fall. A fluidized bed is capable of flowing from a higher level to a lower one, similarly to a liquid.

In appearance, a fluidized bed is similar to a boiling liquid. Each particle is surrounded by streamlets of air, and, therefore, sulphides are roasted very effectively. Heat is to be extracted to maintain temperature at a required point, water coolers being provided for the purpose.

A charge is introduced continuously through a feeding funnel, while at the opposite end of the hearth, at a height of about 1.2 m, the calcine leaves by overflow through a trough. The degree of desulphurization depends on the time the material resides inside the roaster, i.e., on the rate of feeding. Up to 60-70% of the charge are carried off as dust, which is collected and smelted together with the calcine.

For approximately the same dimensions, a multi-hearth roaster handles from 180 to 330 t of concentrates per 24 hours, whereas a fluid-bed roaster is capable of processing 700 to 1400 t. The yield of calcine is respectively 83 and 87%, and the irretrievable copper losses, 0.6 and 0.5%.

Calculation of the Yield and the Composition of Calcine

The method of the present calculation is affected neither by the roasting technique nor the roaster design. First calculated, on the basis of required degree of desulphurization, is the quantity of sulphur to be oxidized. The balance of sulphur is distributed among copper, zinc, lead and iron in the order of decreasing affinity for sulphur. The mineralogical composition thus obtained differs somewhat from the actual one, but it closely approximates the subsequent behaviour of the calcine in smelting.

As an example, let us calculate the yield of calcine for a desulphurization of 65% from a concentrate of the following composition, %: Cu, 14; Fe, 32; S, 38; SiO_2, 4; CaO, 1; Zn, 4; the balance, 6; moisture content, 3.

Let us first express the contents of elements participating in roasting in kilogram-atoms per 100 kg of concentrate. Having divided the respective per cent by the atomic masses, we obtain the quantities of kilogram-atoms per 100 kg of concentrate:

Cu	Fe	S	Zn
0.22	0.57	1.19	0.03

Sulphur that remains after roasting is

$$1.19 - 1.19 \cdot 0.65 = 0.42 \text{ kg-atom}$$

Sulphur in the calcine will be bound into Cu_2S — 0.11 and into ZnS — 0.03, i.e., a total of 0.11 + 0.03 = 0.14 kg-atom.

The balance of sulphur for the formation of FeS is 0.42— —0.14 = 0.28 kg-atom, the amount of FeS thus being 0.28 kmole.

The quantity of iron in the oxide form will be

$$0.57 - 0.28 = 0.29 \text{ kg-atom}$$

Let us assume that because of a small excess of air all of the iron is bound in Fe_3O_4 whose amount is

$$\frac{0.29}{3} \approx 0.1 \text{ kmole}$$

The mineralogical composition of the calcine will be

	Cu_2S	ZnS	FeS	Fe_3O_4	SiO_2	CaO	Balance	Total
kmole .	0.11	0.03	0.28	0.1	—	—	—	—
kg . . .	17.6	0.3	24.6	23.2	4	1	6	76.7

To obtain the elemental composition of the calcine, the contents of elements and oxides should be referred to the yield of the calcine, or the sulphur content multiplied by 0.35. We shall then obtain, %: Cu, 18.3; Fe, 41.8; S, 17.3; Zn, 2.6; SiO_2, 5.2; CaO, 1.3; undetermined, 13.5*

Dust Collection and Gas Cleaning

Dust carried off by gases out of roasters consists of small particles of the charge and other oxides that have condensed from gases on cooling. Dust entrains up to 10% of copper, which is a major value, and this makes it imperative to collect and return it to the processing stages. More than that, roaster gases are utilized for the production of sulphuric acid, the apparatus involved being sensitive even to negligible dust contents. What does much harm and is therefore inadmissible is the presence of arsenic which tends to poison sulphuric acid production catalysts. Consequently, it is essential to complement coarse dust collection by a thorough roaster gas cleaning.

Coarse dust is collected in settling chambers and cyclones, some of it settles out in gas flues on its way to the dust collectors. Gas flues are provided with hoppers and ports to discharge dust.

Settling chambers are built in a variety of configurations, but notwithstanding the type they are local expansions of gas flues. In these chambers gas flow is sharply slowed down, and solid particles settle down by the action of gravity. To improve settling, the path of the gas is sometimes extended inside the chambers by installing baffles (Fig. 25).

In cyclones (Fig. 26) use is made of the centrifugal force that arises when a gas is caused to follow a spiral, vortical path. A gas enters the cyclone at a speed of 15-20 m/s, this resulting in its following a descending spiral path. The

* The quantity of the undetermined substances is found by the difference from 100%; the balance also includes the oxygen of Fe_3O_4.

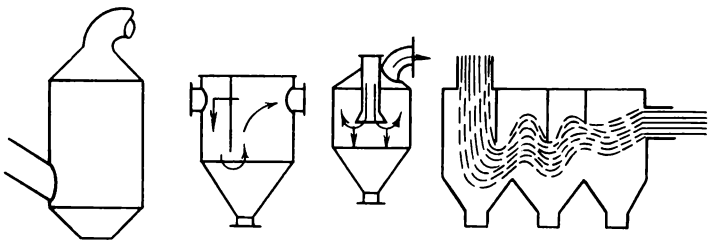

Fig. 25. Settling chambers for collecting coarse dust

centrifugal force pushes the dust particles against cyclone walls, the particles losing speed and falling into a hopper.

Cyclones are built of sheet steel, in heights of 3-4 m and diameters of 0.8-2.5 m. Cyclones are capable of settling out up to 90% of coarse (larger than 5 micrometres) and 30 to 40% of fine dust (finer than 3 micrometres).

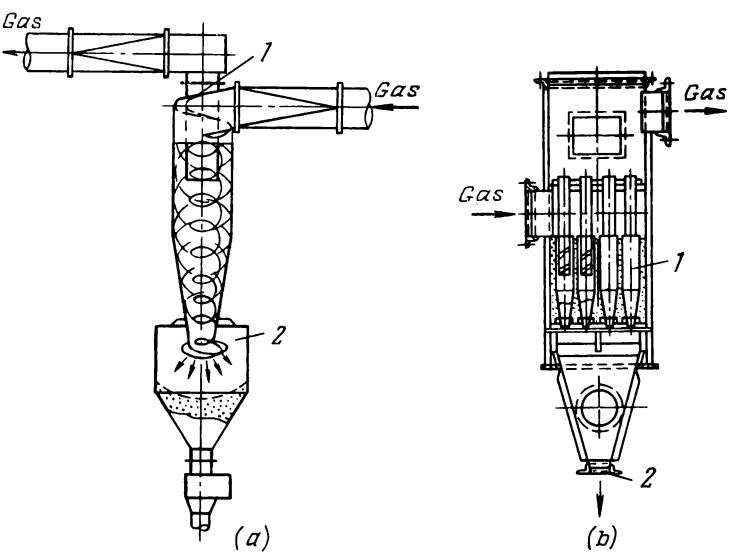

Fig. 26. Design of cyclone (*a*) and group cyclone (*b*)
1—central pipe; *2*—dust hopper

The transversal dimension of the finest particles settled out in a cyclone are governed by the latter's diameter:

$$\alpha_{min} = c\sqrt{D}$$

Constant c depends on the properties of dust and the configuration of cyclone. Collection efficiency increases with smaller cyclone diameters, and this is the reason underlying the use of group cyclones and multi-clones (see Fig. 26).

Fine dust particles, less than 0.5 micrometre across, are not collected in settling chambers and cyclones as finer ones are capable of floating for a long time in a motionless gas, whereas centrifugal forces acting upon fine dust particles are very small due to the latter's small mass. Fine dust particles are formed by condensation of vapours of volatile compounds, in particular, arsenic oxides. Fine dust is removed from gases by the use of electrical precipitators.

Apparatus for electrical gas cleaning, electrical precipitators, consist of separate units, composed each of two metallic electrodes: one with a large surface area, the collecting electrode, and the other with a small surface area, the ionizing electrode. The latter is a vertically suspended wire weighted at its lower end or it is a steel rod. The collecting electrode is either a pipe (tubular electrical precipitators) or two plates that are placed on both sides of a row of wires (plate-type electrical precipitators).

Dust-laden gas moves between electrodes along a wire, from bottom to top, a 50 to 80-kV DC electric field being established between the electrodes. Gas is ionized as it passes between the electrodes and becomes luminescent in the space around the wires, the effect being known as corona.

As they collide with ions, dust particles acquire charges simultaneously with the ionizing electrode and are pushed away from it. Being attracted to the collecting electrode, they give it their charges and settle on it, being no longer affected by electric forces. Collected dust is rapped off the electrodes into a hopper by actuating mechanical hammers at regular intervals of time.

Common types of electrical precipitators can be operated at temperatures up to 450°C and gas flow speeds up to 1 m/s at an efficiency within 98-99%. A schematic diagram of a plate-type electrostatic precipitator is shown in Fig. 27.

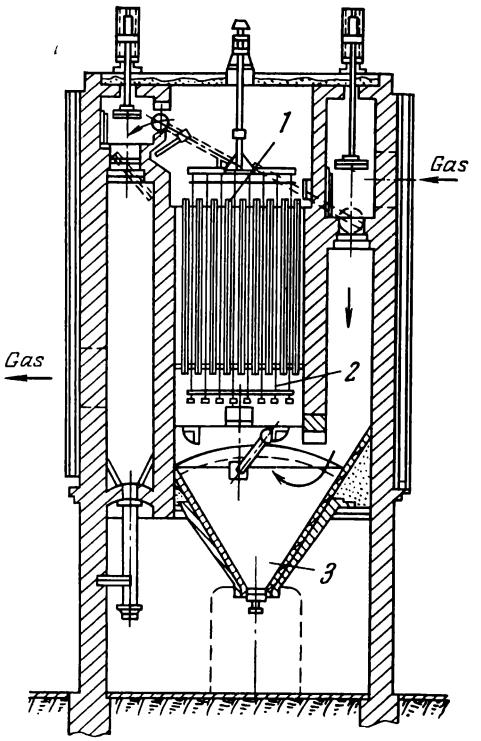

Fig. 27. Plate-type electrostatic precipitators
1—collecting electrodes; *2*—corona discharge electrodes; *3*—discharge of dust

Gases from multi-hearth roasters are cleaned in electrical precipitators, and those from fluid-bed roasters, in cyclones and electrical precipitators. Dust settled out in flues and electrical precipitators is smelted together with the calcine.

15. Matte Smelting from Concentrates

Reverberatory Smelting

Reverberatory Furnace Design

A reverberatory furnace for smelting copper concentrates, shown in Fig. 28, is 35 to 40 m long, up to 11 m wide and up to 4.0 m high. The furnace is built of acid or basic refra-

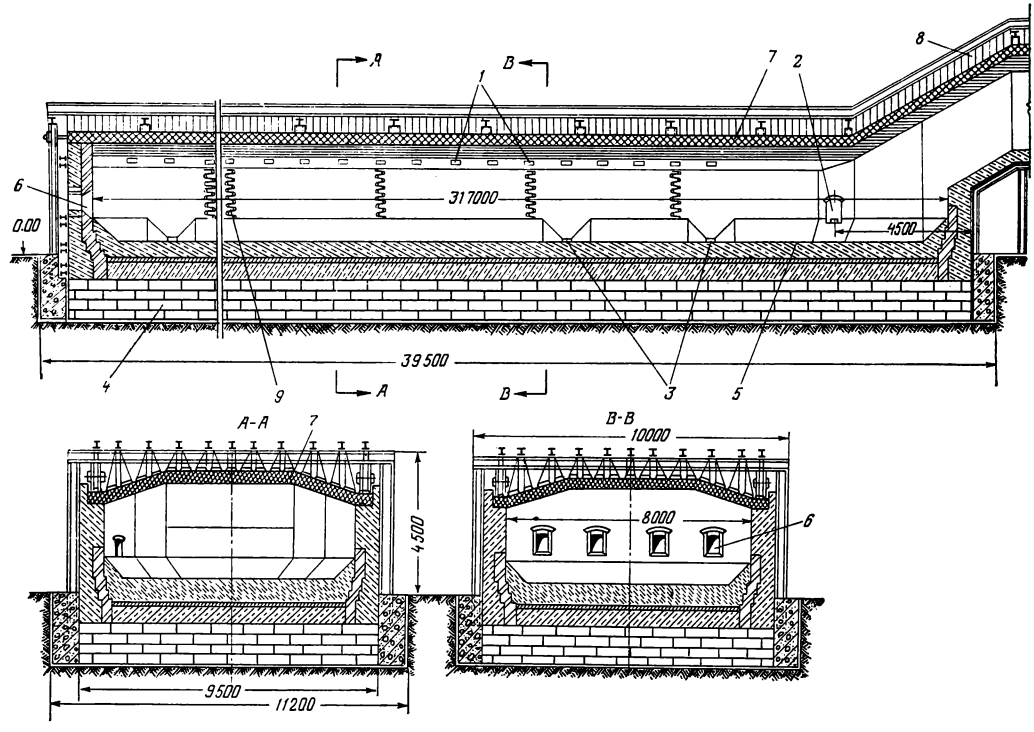

Fig. 28. Reverberatory furnace for smelting copper concentrates

1—feed inlets; *2*—slag port; *3*—matte tap holes; *4*—foundation; *5*—hearth; *6*—burners; *7*—suspended-arch roof; *8*—flue; *9*—expansion joints

ctories depending on whether acid or basic oxides predominate in the charge. Basic refractories are more resistant to basic slags, and acid ones, to acid slags. A correct choice of refractories with due regard to the charge composition ensures a longer service life of the furnace brickwork.

Walls and roof of the furnace are of Dians or magnesite brick. Dians roofs are arched: arched brickwork sets against skewback plates that run along the walls. These roofs are very efficient in smelting of charges rich in SiO_2. It is good practice to smelt charges high in iron in furnaces fitted with suspended (Fig. 28) or sprung-and-suspended arch roofs (Fig. 29) from magnesite or chrome-magnesite brick.

The bottom or the hearth of the furnace is laid from refractory brick in the form of an inverted arch. Formerly hearths were built of Dians brick over which a bed of quartz sand and clay was rammed. The current practice is to lay hearths with chrome-magnesite brick, ram over it a layer of magnesite, then impregnate all this at about 1500°C with a slag high in iron. The slag oxidizes in the process to give off magnetite which seals the brickwork.

Furnace brickwork is reinforced by setting along the walls paired I-beams or riveted columns spaced at 0.9 to 4.2 m. Opposite pairs of beams are drawn together by tie rods above the roof. As the furnace is being heated the tie rod nuts are gradually loosened (Fig. 29).

The thermal expansion of the brickwork is compensated by expansion joints which are voids left in the brickwork (see Fig. 28).

Reverberatory furnaces are heated by natural gas, fuel oil and, a less frequent practice, pulverized coal.

Natural gas or pulverized coal is injected into the furnace by burners, and the fuel oil, by spray burners through openings in the front end wall. Generally, the burners (4 to 10 in all) are set in a single row. Primary air, i.e., air for injecting and atomizing the fuel is heated to 150-400°C and supplied by a fan at a pressure of about 1 kN/m^2. Secondary and tertiary air, heated to 200-250°C, is either blown through annular openings of burners at a pressure of respectively, kN/m^2 (or mm of water): 2(200) and 3(300) or sucked in via holes near the burners (the air is cold in this latter instance).

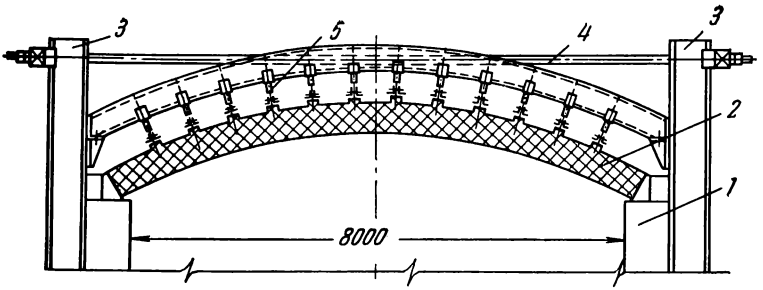

Fig. 29. Sprung-and-suspended-arch roof (after V. I. Smirnov)
1—furnace wall; *2*—arch roof; *3*—buckstays; *4*—tierods; *5*—roof hangers

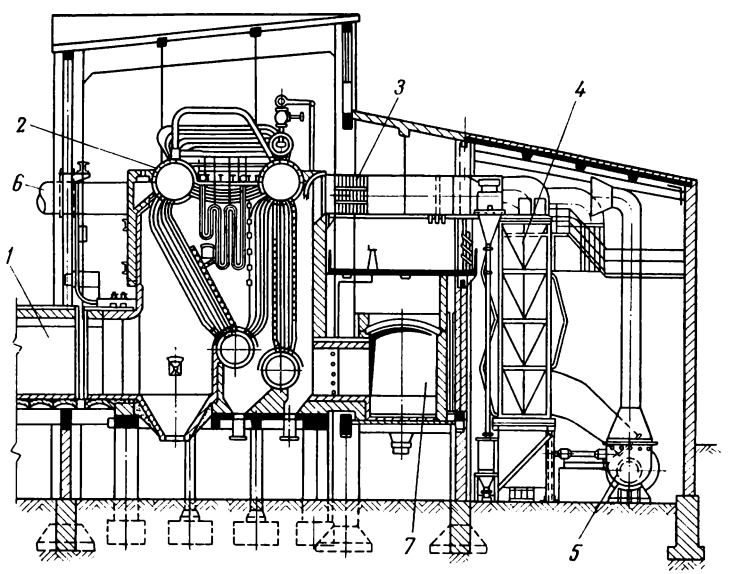

Fig. 30. Utilization of reverberatory furnace gases
1—reverberatory furnace flue; *2*—steam boiler; *3*—ash trap; *4*—air heater; *5*—secondary air fan; *6*—hot air conduit; *7*—stack flue

The heating value of pulverized coal is less than that of fuel oil, and, additionally, coal has a relatively high ash content. Materials are heated in reverberatory furnaces by an open flame. Ash falls upon the surface of the molten bath and may affect the chemical composition of smelting products.

Increased pressure and pre-heating of air improve fuel utilization efficiency.

Temperature of the gases in the furnace at 3 to 10 m from the front wall attains 1600-1550°C, midway inside the furnace it falls to 1400-1350°C, and at the end, to 1250-1200°C.

Thermal efficiency of reverberatory furnaces is very low because of the high temperature of outgoing gases, being not higher than 30%. To improve heat utilization, outgoing gases are passed through waste-heat boilers, then through air heaters (Fig. 30), the efficiency then rising to 55-60%. A waste-heat boiler may generate about 30 tons of steam per hour at a pressure of 10 to 50 atm.

Up-to-date reverberatory furnaces are fitted with apparatus and instruments for automatic control of the temperature in the focus of combustion and in the furnace end. The regulation is based on control of fuel consumption, air supply and draft inside the flue. Automatic regulation of furnace operation brings down fuel consumption by 10 to 11% and increases charge smelting by 6 to 9%.

The charge is fed into the furnace through holes in the roof, arranged throughout the length of side walls. Chutes of charge hoppers, mounted on a working floor above the roof, open up into the holes, the charge introduced into the furnace forming banks along the walls to protect them against exposure to molten slag and hot gases.

Molten slag is poured into the furnace via a launder entering a port in the front or side wall of the front part of the furnace.

Matte and slag are drawn off as they accumulate. The slag port is located in the end part of the furnace at a height of about 1 m from the hearth. Slag is maintained at a required level by a dam of refractory clay. There are two tapholes for matte, both are located in a side wall at the hearth level. The taphole arrangement includes a cast iron or copper plate

with square holes for receiving cast iron thimbles (the taphole proper) of inside diameters of 45 to 50 mm. Tapholes are stopped by plugs from refractory clay, set on an iron bar.

The current Soviet practice is to use the more convenient siphon matte tapping (Fig. 31). The siphon is a canal in

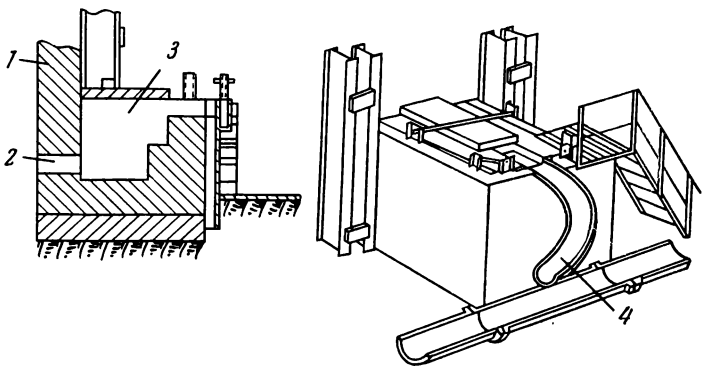

Fig. 31. Siphon for tapping matte from reverberatory furnaces (after V. I. Smirnov)
1—longitudinal furnace wall; *2*—siphon canal; *3*—siphon outlet; *4*—launder

furnace brickwork which connects the bath with the pit outside the furnace. The outlet from the siphon is stopped by a refractory clay plug, which is pierced with the aid of an iron bar whenever matte is to be tapped.

Roasted Concentrate Smelting

A charge of concentrate and fluxes, proportioned prior to roasting, is thoroughly roasted and mixed inside the roaster and discharged while hot. It is desirable to utilize this heat in smelting, but the transportation and the feeding of a hot charge presents problems since the evolving gases tend to cause a heavy formation of dust. In order not to lose the sensible heat of the calcine, roasters are sometimes located directly above the reverberatory furnaces, and, if this is not feasible, the charge is fed cold with the use of various powered feeders and conveyors.

As the charge is heated in the reverberatory furnace, copper and higher iron oxides are reduced and slag is formed

$$6CuO + FeS \rightarrow FeO + 3Cu_2O + SO_2 \quad (79)$$

$$2FeS + 6Fe_2O_3 + 7SiO_2 \rightarrow 7Fe_2SiO_4 + 2SO_2 \quad (80)$$

$$FeS + 3Fe_3O_4 + 5SiO_2 \rightarrow 5Fe_2SiO_4 + SO_2 \quad (81)$$

Silicates melt (65) and dissolve other oxides while trickling along the banks of material inside the furnace to form a slag.

Copper and iron sulphides melt to give a primary matte which is impoverished in iron and enriched in copper as it trickles down the banks of material

$$[2FeS] + (2Cu_2O) + (SiO_2) \rightarrow [2Cu_2S] + (Fe_2SiO_4)^* \quad (82)$$

These and other reactions of reverberatory smelting require a simultaneous participation of three or more starting substances, and, therefore, a thorough mixing of burden in roasting facilitates smelting.

In smelting, sulphide sulphur in the charge is oxidized chiefly by the oxygen of the higher oxides and, to a lesser extent, by the oxygen of furnace gases, since the gases usually carry very little excess oxygen. It is assumed that some 20 to 25% of the sulphur that remains in a roasted concentrate are oxidized in the course of smelting.

Noble metals, gold and silver are well soluble in molten mattes, their solubility in slags being negligible. It is, therefore, a major economic advantage to use gold-bearing ores, their concentrates and other auriferous materials as fluxes since the noble metals they contain will be recovered at practically no cost. The charge is composed prior to roasting to ensure its mixing and heating by the heat of oxidation of sulphides.

Reactions between iron oxides and sulphides have a major bearing upon smelting efficiency since Fe_3O_4 and other ferrites should be reduced as completely as possible because they are poorly soluble in slags. If reduction of ferrites does not go to completion at the banks, it continues inside

* Here and further on, matte components are enclosed in square brackets, and the slag components, in round brackets.

the melt at the matte-slag interface. The evolving sulphurous gas bubbles carry with them matte droplets to the slag layer. Slags that entrain unsettled matte are bound to be rich in copper.

Investigations by A. Vanyukov and other authors have shown that dissolved magnetite is responsible for a greater loss of copper in slag because, among other reasons, magnetite induces higher solubility of copper in slag. Roasted concentrates always carry much trivalent iron in the form of Fe_3O_4 and Fe_2O_3, particularly, after fluid-bed roasting where oxides have less possibility to be reduced by residual sulphides. Much trivalent iron is introduced by converter slag, and this will be discussed below.

The composition of matte obtained in smelting depends on desulphurization in roasting and smelting, and roasting can be calculated by assuming a composition for matte, an example being given below.

Roasted and smelted is a copper concentrate of the following composition, %: Cu, 14; Fe, 32; S, 38; SiO_2, 4; Al_2O_3, 5; CaO, 1; undetermined, 3; moisture content, 3.

A matte with 30% Cu is required. In accordance with the V. Mostovich rule, the matte should contain 25% S, the content of undetermined components being assumed equal to 10%.

Therefore, the amount of iron in the matte will be, %:

$$100 - (25 + 30 + 10) = 35$$

Recovery of copper into matte in reverberatory smelting is taken to be 95%. Then the amount of copper passing from 100 kg of concentrate into matte will be

$$\frac{14 \cdot 95}{100} = 13.3 \text{ kg}$$

The amount of matte will be

$$\frac{13.3 \cdot 100}{30} = 44.4 \text{ kg}$$

The amount of sulphur in the matte will be

$$\frac{44.4 \cdot 25}{100} = 11.1 \text{ kg}$$

If it is assumed that 20% of the charge sulphur are oxidized in smelting, the amount of sulphur to be left in the charge will be

$$\frac{11.1 \cdot 100}{80} = 13.9 \text{ kg}$$

The amount of sulphur to be oxidized in roasting will then be

$$38 - 13.9 = 24.1 \text{ kg}$$

Hence, the required degree of desulphurization will be

$$\frac{24.1}{38} \cdot 100 = 63.3\%$$

SMELTING OF RAW (NON-ROASTED) CONCENTRATES

Sulphide concentrates are smelted raw, if their sulphur content is low, if no sulphuric acid is produced or if they are smelted in combination with either oxidized or mixed concentrates.

A charge of concentrates and a small amount of fluxes is thoroughly stirred in mixers and fed to the furnace. As the charge is heated on the banks, it gives off sulphur of higher sulphides. The sulphur immediately oxidizes and is carried away by outgoing gases in the form of SO_2. Desulphurization may be as high as 45 or 50%. Reactions between sulphides and oxides are possible, but they are not characteristic of the smelting technique, since the charge carries a relatively small quantity of oxides.

Characteristic of raw concentrate smelting is a large consumption of fuel (as the furnace is charged with cold and often moist materials), a somewhat lesser dust entrainment and a lower capacity. In the smelting of raw concentrates, sulphur is mostly lost, polluting the surrounding locality. The chief advantage in raw concentrate smelting is a reduction in losses of copper and gold. The largest plants of the Soviet Union, USA, Chile and Africa operate on pre-dried raw (non roasted) charge.

If the concentrate in the above calculation is smelted raw with a desulphurization of 50%, the amount of sulphur passing from 100 kg

of concentrate to matte will be

$$\frac{38 \cdot 50}{100} = 19.4 \text{ kg}$$

The quantity of matte will be

$$\frac{19.4 \cdot 100}{25} = 77.6 \text{ kg}$$

The matte will carry

$$\frac{14 \cdot 95}{100} = 13.3 \text{ kg of copper}$$

or

$$\frac{13.3 \cdot 100}{77.6} = 17.1\%$$

The calculations show that a roasting of concentrates results in smelting of a richer matte.

SMELTING PRODUCTS AND PERFORMANCE

Matte is tapped through a siphon (or tapholes, should a fault in siphon arise). The tapholes are more difficult to open as the operation often requires burning through of the plugs by electric current or oxygen.

Matte runs along a launder into a ladle which is transported by an overhead crane to the smelter converting department.

Mattes high in copper are a disadvantage in reverberatory smelting as they entail greater physical and mechanical losses of copper in the slags, and copper smelters currently limit copper content of mattes to 20-40%.

Slag is drawn off at regular intervals through the slag port by removing the dam of refractory clay. Slag flows along runners into a ladle, and is then dumped or granulated*. If the granulated slag is free from copper companion values, it is used in building or for back-filling mine workings. Sometimes slag is cast into blocks for use in road or civil construction.

By mass, the yield of slag in reverberatory smelting approximates that of matte or exceeds it, but never by a factor greater than 2. The quantity of slag governs the

* Granulation is a breaking of molten slag into grains, or granules, by a water jet.

absolute copper loss of and the consumption of fuel and fluxes. Enrichment of blast in oxygen, currently practised by some plants within the limits of up to 35% O_2, besides improving fuel efficiency, reduces the amount of outgoing gases and dust entrainment. It also allows a lesser consumption of fluxes, and, consequently, a lesser fall of slag, as the higher melting point of such a slag has no adverse effect because of a higher working temperature inside the furnace. Shortcomings of blast oxygen enrichment are greater wear of the furnace lining and higher consumption of refractories.

A comparison of roasted and raw charge smelting performance is given below:

	Roasted charge	Raw charge
Furnace capacity, t/m² (24 hours)	5-8	2.5-5
Recovery of copper and noble metals to matte, %	93-94	95-99
Consumption of reference fuel, % . . .	14-15	19-20
Copper and slag content, %	0.40-0.60	0.25-0.40

In current world practice, approximately seven times as much copper is smelted from raw charges (sometimes predried to 5-6% residual moisture content) than from roasted ones.

Approximate compositions of reverberatory smelting slags at different plants are given below, %:

Cu	0.30	0.44	0.25
SiO_2	37.4	32.0	35.0
FeO	36.0	44.8	38.6
CaO	4.2	6.0	5.0
Al_2O_3	8.3	10.2	10.1
MgO	2.0	0.4	—
ZnO	1.0	—	—
S	3.5	2.0	—

The major properties of slags are governed mainly by the ratio of the three chief constituents: SiO_2, FeO and CaO.

In order to minimize consumption of fluxes and, in consequence, the yield of slag, slag composition for the charge calculations is assumed on the basis of practical data from operating smelters and as close as possible in the ratio of chief constituents to the gangue of the concentrate.

This approach may be exemplified by a charge calculation that follows.

Calculate the charge for the smelting of a calcine whose composition, as determined previously, is, %: Cu, 18.3; Fe, 41.8; S, 17.3; SiO_2, 5.2; CaO, 1.3; the balance, 13.5.

Composition of fluxes available locally, %, is:

Constituents	SiO_2	Fe	Al_2O_3	CaO	Loss in heating	The balance
Gold-bearing quartz	90.0	3.0	3.0	1.0	1.0	2.0
Limestone	3.0	1.0	1.0	52.0	42.0	1.0

The yield and the composition of the resulting matte have been determined above. 100 kg of raw concentrate yielded 76.7 kg of calcine, the latter's smelting being 44.4 kg of matte which contained 30% Cu, 35% Fe, 25% S, 10% undetermined. Therefore, the fall of the same matte from 100 kg of calcine will be

$$\frac{44.4 \cdot 100}{76.7} = 57.9 \text{ kg}$$

The blowing of the matte in a converter results in a converter slag (see page 149) which is returned to reverberatory smelting. Assume the slag composition to be, %: SiO_2, 26; Fe, 50 (FeO, 64.3); Cu, 2; undetermined, 22.

The yield of converter slag can be roughly determined by assuming that all of the iron will pass to it from matte

$$\frac{57.9 \cdot 35 \cdot 100}{100 \cdot 50} = 40.6 \text{ kg}$$

In the reverberatory furnace the converter slag copper yields an additional quantity of matte

$$\frac{2 \cdot 40.6 \cdot 0.95 \cdot 100}{100 \cdot 30} = 2.6 \text{ kg}$$

The total quantity of matte will be

$$57.9 + 2.6 = 60.5 \text{ kg}$$

Next, determine the quantity of substances, that pass to slag by making use of calculation Table 10. The ratio of SiO_2, FeO and CaO obtained is dissimilar to compositions of typical slags, this pointing to a necessity to add fluxes to the charge.

Referring to data on page 132, let us choose a slag of the following composition (rounded off): 32% SiO_2, 45% FeO (35% Fe), 6% CaO; 17% undetermined.

To determine the consumption of fluxes, let us draw up the slag formation balance (Table 11) in the form of equations, the consumption of quartz flux being designated by x, that of limestone by y; and the yield of slag by z.

	To be slagged, kg		Contained in quartz flux, kg		Contained in limestone, kg		Passes to slag, kg
Fe	40.9	+	$0.03x$	+	$0.01y$	=	$0.35z$
SiO_2	15.8	+	$0.9x$	+	$0.03y$	=	$0.32z$
CaO	1.3	+	$0.01x$	+	$0.52y$	=	$0.06z$

Table 10

Charge Calculation Table

Material	Mass, kg	Content of elements or oxides									
		Cu		Fe		S		SiO_2		CaO	
		%	kg	%	kg	%	kg	%	kg	%	kg
					In						
Calcine	100.0	18.3	18.3	41.8	41.8	17.3	17.3	5.2	5.2	1.3	1.3
Converter slag	40.6	2.0	0.8	50.0	20.3	—	—	26	10.6	—	—
Total	140.6		19.1	—	62.1	—	17.3	—	15.8	—	1.3
					Out						
Matte	60.5	30.0	18.2	35.0	21.2	25.0	15.1	—	—	—	—
Gas and dust	—	—	0.5	—	—	—	2.2	—	—	—	—
To be slagged	74.7	0.5	0.4	54.8	40.9	—	—	21.2	15.8	1.7	1.3
					FeO						
				73.5	52.6						
Total	—	—	19.1	—	62.1	—	17.3	—	15.8	—	1.3

Note. When determining the quantity of substances passing to dust and gases, we assume: (a) copper losses are distributed evenly between dust and slag; (b) sulphur that has not passed to matte burns to SO_2.

Having eliminated z and solving the system of the equations, we find: $y = 10.8$, $x = 24.5$.

We check on the calculation by drawing up the balance sheet of the heat/melt (Table 11).

An example of the calculation of the required number of reverberatory furnaces and of their size is as follows: let us continue the calculation given above by determining the number and the size of reverberatory furnaces necessary to smelt 4000 tons of concentrate per day (see Table 11).

The yield of calcine from the concentrate is 76.7%. The required smelting capacity in terms of calcine is

$$\frac{4000 \cdot 76.7}{100} = 3068 \text{ t}$$

The quantity of quartz flux required per day

$$\frac{3068 \cdot 24.5}{100} = 752 \text{ t}$$

and that of limestone,

$$\frac{3068 \cdot 10.8}{100} = 332 \text{ t}$$

The daily amount of solid charge will be

$$3068 + 752 + 332 = 4152 \ t$$

The specific smelting capacity for a roasted charge may be assumed equal to 7.0 t/m² per 24 hrs, the required hearth area of the reverberatory furnace then being

$$\frac{4152}{7.0} = 593 \text{ m}^2$$

The hearth area of modern reverberatory furnaces commonly ranges from 180 to 330 m². We then assume that the above 593 m² of hearth area will be materialized in two 35-m long reverberatory furnaces of 297 m² each. The furnace width will thus be

$$\frac{297}{35} = 8.43 \text{ m}$$

In accurate calculations, where the choice of the specific smelting capacity is given a thorough substantiation, account should be taken of a month-long shutdown of reverberatory furnaces every year for overhaul.

Table 11

Charge and Smelting Products Balance Sheet

Material	Mass, kg	Cu		Fe		S		SiO_2		CaO	
		%	kg	%	kg	%	kg	%	kg	%	kg
				In							
Calcine	100	18.3	18.3	41.8	41.8	17.3	17.3	5.2	5.2	1.3	1.3
Converter slag	40.6	2.0	0.8	50.0	20.3	—	—	26.0	10.6	—	—
Quartz flux	24.5	—	—	3.0	0.7	—	—	90.0	22.0	1.0	0.2
Limestone	10.8	—	—	1.0	0.1	—	—	3.0	0.3	52.0	5.6
Total		—	19.1	—	62.9	—	17.3	—	38.1	—	7.1
				Out							
Matte	60.6	30.0	18.2	35.0	21.2	25.0	15.1	—	—	—	—
Slag	119.5	0.3	0.4	35.0	41.7	—	—	32.0	38.1	6.0	7.1
Gases	—	—	0.5	—	—	—	2.2	—	—	—	—
Total		—	19.1	—	62.9	—	17.3	—	38.1	—	7.1

Other Methods of Copper Concentrate Smelting

Flash Smelting

Copper smelting requires the interaction between sulphides and oxides which is possible in their mutual contact on the banks or in the bath of reverberatory furnace. The designation "Flash Smelting" is a conventionality, since the technique differs from the common smelting methods by the injection of a raw concentrate into a reverberatory furnace by oxygen or pre-heated air. Sulphides are roasted while the particles are in flight, this resulting in a high desulphurization which may attain 75%. The released heat raises the temperature of the furnace space. When oxygen blast is used, the liberated heat is sufficient to melt the charge and overheat the melt, no fuel is required, the technique is often termed *autogeneous*. Because of the absence of nitrogen, the quantity of outgoing gases is small, and they contain up to 75% SO_2. After removal of dust from the gases, sulphurous anhydride can readily be liquefied and bottled and made available to a variety of consumers, e.g., paper manufacturing plants. If the concentrate is injected by an air blast, the path of the particles is made longer by providing a cylindrical shaft above the front part of the furnace, the air being preheated by outgoing gases to 500°C, some fuel (about 2% of the mass of the charge) being burned to stabilize furnace operation. The outgoing gases at a temperature of about 1300°C pass through a dust settling chamber, waste-heat boilers, a heat exchanger for preheating the blast, an electric precipitator and enter a sulphuric acid plant having a 10% content of SO_2.

Before the concentrate is injected into the furnace, it should be dried to avoid lumping either in rotary drying kilns or in a vertical pipe drier, which is an original technique developed in the Soviet Union. The concentrate is injected into the pipe drier from below at a speed of 50 m/s by gases heated to 600°C. Sufficiently fine particles from its top end pass into dust collectors, then to devices that inject them into the furnace. Coarse particles that settle out at the bottom are re-ground.

Owing to a high desulphurization, flash smelting yields very rich mattes, containing up to 50-60% copper and slags, correspondingly high in copper, 1 to 1.6% Cu, which are treated for copper recovery similarly to converter slags (see Para. 17), both slags being analogous in high magnetite percentage. Specific smelting capacity of flash smelting may be as high as 13 t/m^2.

Electric Furnace Smelting

This smelting technique has been the subject of investigation at the beginning of this century in Russia, France and USA and has been introduced industrially for the first time in Norway in 1928.

The chemistry of electric furnace smelting is the same as that of reverberatory smelting of a roasted charge, the only difference being that the latter is smelted by the heat of an electric current that passes through a layer of slag between the immersed carbon electrodes. The design of electric furnaces for copper and for nickel smelting is identical. As the latter applications are more numerous, the furnaces are discussed in detail in Para. 23.

Desulphurization in electric furnaces is possible only through the agency of the oxygen of oxides in the charge, which is generally roasted if it carries much sulphur.

The possibility of obtaining high temperatures allows operation on relatively high-melting slags, at a low flux consumption. The yield of slags is fairly low, their copper contents lying between 0.15 and 0.40%, and, therefore, copper recovery to matte is generally not lower than 97%.

As the furnaces are air-tight and the amount of gases is small, dust entrainment is low, this allowing a ready recovery of volatilized values and high concentrations of SO_2.

Consumption of refractories in electric furnaces is lower than that in the reverberatory furnaces and their operating periods are greater by a factor of 3 to 5.

Notwithstanding its advantages, a prerequisite of electric smelting is a sufficiently cheap electric power whose sources should not be more than 1000 or 1500 km away. Consumption of electric power per ton of charge is 380 to 490 kW-h depending on its fusibility and moisture content.

Standard in the Soviet Union are furnaces rated at 30 or 50 megawatts, their hourly capacity ranging from 60 to 150 tons of charge.

The consumption of electric power per ton of blister copper ranges from 1500 to 2300 kW-h, this being equivalent to 185 to 200 kg of reference fuel, and, therefore, by 7 or 8 times less than that in reverberatory smelting.

16. Smelting of Matte from Ores

Smelting of a reasonably rich matte from a 2 or 3% Cu ore, requires the slagging of almost all of the iron the latter contains. In its turn, this calls for the oxidation of the sulphur that is bound to iron, i.e., for a high degree of desulphurization. A preliminary roasting of ore is unfeasible because it would have required the crushing of all the ore. For this reason ore sulphur is oxidized in the course of smelting, this being effected in blast furnaces whose heights are much greater than their widths.

Shaft Furnace Arrangement

A copper smelting blast furnace (Fig. 32) is a high shaft that is filled with a mixture of lump ore, fluxes and coke. Air necessary for the combustion of fuel and oxidation of sulphides is injected through tuyeres located in the lower part of the furnace. Furnace walls are of water jackets, or flat iron boxes, welded from sheet boiler steel, that are cooled by running water. The refractories are a crust of the materials being smelted which freeze on the inside walls of water jackets that face the furnace working space. The base of the furnace, a rectangular cast iron plate, is installed on steel columns or jacks set on a foundation.

The water jacketed part of the furnace is a trapezium in cross-section, the smaller base being at the bottom. The end face water jackets, each shaped as a rectangular trapezium, are set in pairs vertically. Furnace cross-section in plan is rectangular, at tuyere level the width being 1.4 m, and the length, up to 15 m. The height from the hearth to the top is about 7 m.

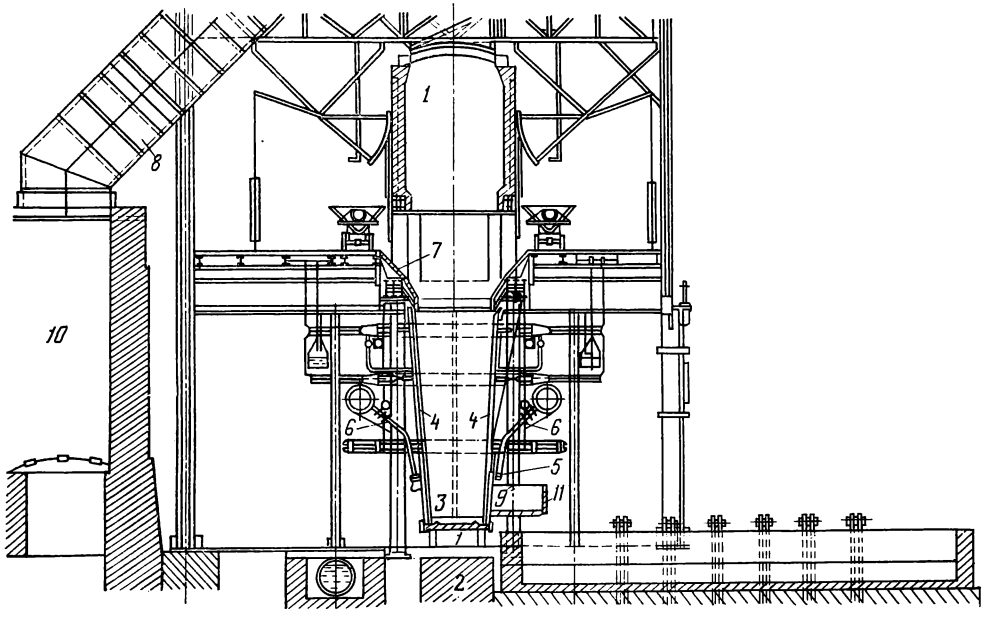

Fig. 32. Blast furnace for copper smelting

1—hood; *2*—foundation; *3*—hearth; *4*—water jackets; *5*—tuyeres; *6*—tuyere pipes; *7*—charging plate; *8*—flue; *9*—tapping hole; *10*—dust settling chamber; *11*—runner

The blast is injected into the furnace via tuyeres, secured to water jackets and connected to a bustle pipe.

The charge of ore, fluxes and coke is fed from the top to a level somewhat lower than the top edge of water jackets. The high column of charge should be effectively permeable to the gases, and, therefore, ore, fluxes and coke are charged as large lumps, 25 to 100 mm across.

The chief source of heat is the oxidation of pyrite of the copper ore. In the presence of quartz, pyrite oxidizes according to the reactions

$$2FeS_2 + 5O_2 \rightarrow 2FeO + 4SO_2 = 1379 \text{ kj (330 kcal)}$$
$$2FeO + SiO_2 \rightarrow Fe_2SiO_4 = 35 \text{ kj (8.4 kcal)}$$

$$2FeS_2 + 5O_2 + SiO_2 \rightarrow Fe_2SiO_4 + 4SO_2 = 1414 \text{ kj (338.4 kcal)} \quad (83)$$

The oxidation of 1 kg of pyrite liberates the following amount of heat, kj

$$\frac{1414 \cdot 1000}{2 \cdot 120} = 5890$$

where 120 is the molecular mass of FeS_2 which is equivalent to the heat of combustion of $\frac{5890}{27\,200} = 0.21$ kg of coke

It should be stressed, that before burning the pyrite partly dissociates with an evolution of sulphur vapours and part of FeO oxidizes to Fe_3O_3 and Fe_3O_4. However, this may be overlooked in a rough evaluation of pyrite heat value. The amount of heat released in the combustion of pyrite is sufficient to melt the charge if the content of pyrite in the ore is above 75%. Such ores are very rare, and, therefore, an additional source of heat is the carbon of the coke which burns according to the reaction (44)

At the centre of combustion (in the bottom part of the furnace, near the tuyeres), the temperature attains 1400-1450°C, the heat is transmitted upwards throughout the height of the furnace shaft.

Melting begins in layers of the charge where the temperature is approximately 1000°C. Iron and copper sulphides

that have not yet oxidized melt out of lumps of ores leaving behind them a porous framework of quartz and oxides of iron, calcium, magnesium and aluminium.

The readily fusible alloys of SiO_2, CaO and FeO melt at 1100°C. As they trickle down, they dissolve gradually other gangue oxides.

The porous mass of solid oxides resulting from the melting of easy melting constituents plays a major part in smelting. A molten stream of sulphides meets inside the pores of the mass the ascending hot oxygen-bearing gases, the essential smelting reactions (79, 80, 81, 82) taking place intensively over a large area of contact and at a high temperature.

The molten mixture of sulphides and silicates trickles down and is continuously run off to a settler, oval in plan, whose axis is perpendicular to the longer axis of the furnace. The settler is a steel sheet shell lined with chrome magnesite brick or talc stone. The molten mass from the furnace separates into matte and slag during the time it resides inside the settler. Slag is allowed to flow out along a launder at the end of the settler opposite the inlet hole. The matte is drawn off through tapholes in the side walls at hearth level.

Gases are exhausted through a fireclay brick hood, which is reinforced by a metallic framework and tops the furnace above the charging platform level. The hood's side walls are fitted with charging ports that are closed by hinged doors. Gas exhaust steel pipes, lined on the inside with refractory brick, branch off the roof of the hood to channel the gases to the dust chamber. In some furnaces, the hoods are water-cooled.

The charge always carries an amount of fine particles. At the same time, as the charge melts, its column descends, the lumps being ground and disintegrated in the process. The gases that are injected at the bottom permeate at a great speed the charge and carry away finer particles. Dust entrainment may be as high as 5% of the mass of the charge.

The dust settles out inside the flues and the dust chamber, whereas the finer particles and the sublimates are collected

by electric precipitators*. As to chemical composition, the dust is close to the ore, and it is processed in reverberatory furnaces in combination with copper concentrates.

Recovery of copper to matte in the blast furnace smelting is 78-87%. Such a low recovery is due to a large yield of slag per unit mass of matte. The specific smelting capacity per 24 hours is capacity referred to 1 m^2 of the furnace cross-section area at tuyere level, its value ranges from 38 to 52 t/m^2 per 24 hours with coke consumption of 2 to 3% of the charge mass. Smelting capacity may be boosted to 90-150 t/m^2 per 24 hours by increasing the coke consumption and/or by oxygenating and preheating the blast.

Charge feeding and removal of smelting products are today mechanized at all plants. The task of the coming years is to make the furnace operation automatic, i.e., to automatically control the blast pressure as a function of the charge height and outgoing gas temperature.

Copper content in blast furnace mattes varies from 15 to 25%, but rich ores may sometimes produce mattes as high as 45-50% Cu. Slags carry 0.12 to 0.35% of copper, the common content being about 0.3%.

The run of blast furnaces may be anywhere between 4 and 18 months, 10 or 12 months being the average.

Charge calculations for a blast furnace smelting are similar to those of the reverberatory smelting, except for the slag composition choice which is much more limited, the relatively lesser input of heat making it essential to bring down flux consumption to a lowest possible level. On the average, blast furnace slags run 30 to 39% SiO_2, 40 to 55% FeO and 4 to 12% CaO.

As no ore dressing is involved, some values of complex ores, i.e., zinc, lead, molybdenum and other copper associates are lost with the slags and gases. Blast furnace gases are low in sulphurous anhydride and, therefore, cannot be used for sulphuric acid manufacture. By contrast, the blast furnace smelting requires less fuel and less amount of costly refractories and much less floorspace than reverberatory furnaces.

* Sublimates are fine particles condensed from vapours of metallic compounds.

Orkla Smelting Technique

This is a variety of blast furnace smelting which allows the manufacture, directly from ores, of elemental sulphur which is in great demand by many industries.

Orkla smelting furnaces are somewhat higher, 8 to 8.5 m than standard blast furnaces and are water-jacketed in their lower half only. The upper portion of the shaft is a metal jacket lined with fireclay brick. Furnaces have no hood, but are spanned by roofs fitted with an air-tight charging arrangements at their centre. Inside faces of water jackets are lined with a thin coat of refractory brick.

The Orkla technique is used to smelt, along with lump sulphide ore, briquettes of fines and coke, the binder being lime and tripoli. A moisted mixture is briquetted at a pressure of 150 kg/cm^2. The briquettes are strengthened by ageing in the air. The furnace is charged with fine (20-30 mm) coke, 12% of the mass of the charge, which is a vigorous reducing agent because of its large surface area.

Matte and slag separate into layers in the lower part of the furnace (internal settler), the process being completed in the external settler. This allows to maintain a neutral or slightly reducing atmosphere inside the furnace shaft.

The orkla smelting may be described by the chemical reactions that are already known to us (reactions 79 through 83).

At the tuyeres, coke carbon burns to CO_2, and sulphide sulphur is also partly oxidized. Gases, containing SO_2, CO_2, free oxygen and nitrogen, ascend inside the shaft to permeate the charge column. Free oxygen is gradually consumed in the oxidation of sulphides and combustion of carbon. Carbon dioxide interacts with carbon to give CO (reaction 4), whereas the moisture of the blast and the charge is either decomposed by carbon or interacts with sulphides to give hydrogen sulphide

$$H_2O + C = CO + H_2$$

$$FeS + H_2O = FeO + H_2S$$

Thus, as the gas moves upwards its composition suffers changes, the contents of CO_2, O_2 and H_2O decreasing because

of the formation of carbon monoxide, sulphurous gas and hydrogen sulphide. As sulphurous gas rises inside the shaft it is reduced to sulphur

$$2SO_2 + 4CO \rightarrow S_2 + 4CO_2 \quad (84)$$

Subsequent interaction of sulphur vapours with carbon and carbon monoxide partly produces carbon oxysulphide and carbon bisulphide

$$2CO + S_2 \rightarrow 2COS$$

$$C + S_2 \rightarrow CS_2$$

Sulphur vapours from dissociation of pyrite and other higher sulphides pass to gas at the top of the charge column.

The composition of top gases is approximately as follows, g/m^3: S_2, 290; SO_2, 28; H_2S, 20; ($COS + CS_2$), 19.

The gases should leave the furnace at a relatively high temperature (430-450°C) in order to allow collection of dust before sulphur vapours condense. Coarser dust settles out mainly in a gas header and flues, final removal of dust being effected by electric precipitators.

Clean gas is channeled to contact chambers filled with a porous catalyst composed of alumina cement and aluminium hydroxide. Elemental sulphur vapours result from the interaction of gas mixture constituents in the presence of the catalyst at a temperature of about 450°C

$$2SO_2 + 2CS_2 \rightarrow 2CO_2 + 3S_2,$$

$$2SO_2 + 4H_2S \rightarrow 4H_2O + 3S_2,$$

$$2SO_2 + 4COS \rightarrow 4CO_2 + 3S_2.$$

The gases are next passed underneath the water-tube boilers. Sulphur condenses upon the tubes and trickles into a collector. Heat liberated in its condensation is utilized to produce low-pressure steam.

In the condensation, the gases are cooled approximately to 120°C. Fine droplets of sulphur floating in the gas are collected in spray towers in which the gas is fed from the bottom upwards in countercurrent to molten sulphur which trickles down along the checkerwork.

Gas treatment flowsheets differ with the plants, one of the plants being shown in Fig. 33.

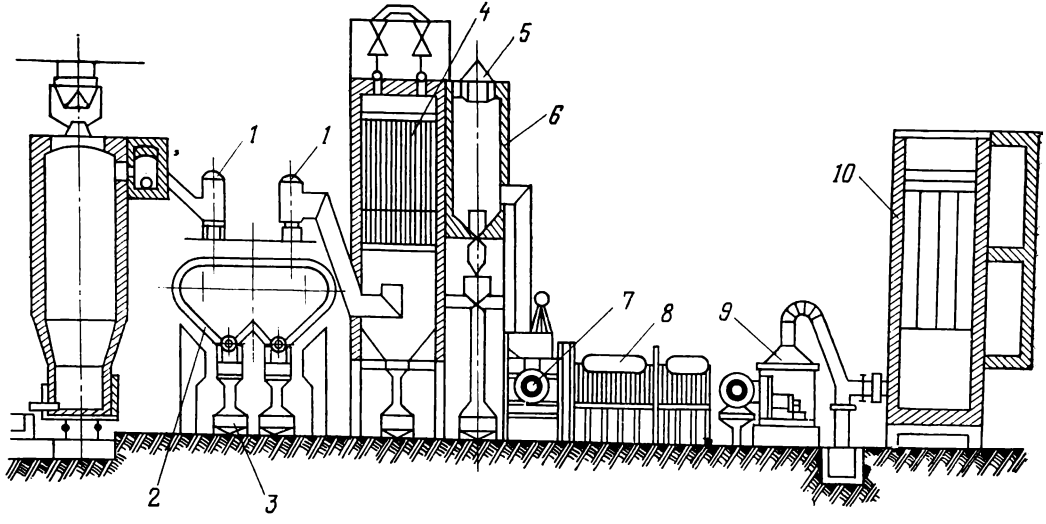

Fig. 33. Orkla process smelting

1—flue; *2*—gas header; *3*—dust discharge; *4*—electrostatic precipitator; *5*—charging of catalyst; *6*—contact chamber; *7*—flue; *8*—cooler; *9*—spraying tower; *10*—heat exchanger

Orkla process mattes contain but 5-10% copper. To facilitate subsequent processing, these mattes are enriched in copper through a concentration smelting in a usual blast furnace, which is similar to an ore semi-pyritic smelting: matte iron oxidizes and passes to slag, this raising matte copper content to 25-40%.

The orkla smelting process is inferior to the usual blast furnace in capacity. Besides, it requires more coke. Specific smelting capacity does not exceed 35-40 t/m^2 of furnace cross-section area at the tuyeres, and coke consumption is 10-12% of the mass of the charge. Poorer matte smelting performance is recouped for by the resulting elemental sulphur whose recovery from gases attains 88.5%.

17. Converting

In modern copper manufacturing practice abroad, the importance of various smelting techniques, in terms of the mass of copper their mattes contain, may be evaluated by the data below, %:

Reverberatory smelting	79
Blast furnace smelting	15
Electric furnace smelting	1
Flash smelting	5
Total	100

The mattes differ from one another in contents of copper and iron only.

Approximate compositions of mattes are given in Table 12.

Table 12

Compositions of Mattes Smelted from Ores and Concentrates

Smelting technique	Content in the matte, %						
	Cu	Fe	S	SiO_2	CaO	Al_2O_3	Zn
Blast furnace	16	49	24	2	—	1	1
Reverberatory	25	36.9	24.5	1	1	1	3.9
Electric furnace	30	38	23.9	1.5	0.6	1.8	2.6

Irrespective of the technique by which a matte has been smelted from ores or concentrates, its subsequent processing to blister copper, or converting, is the same.

Converter Arrangement

A modern copper production converter (Fig. 34) is a horizontally mounted cylindrical shell with tuyeres located along its generatrix.

Converter shell is lined on the inside with magnesite and chrome-magnesite brick. The shell carries two smooth and one toothed rims, the smooth rims being supported by sets of carrying rollers, mounted in swivelling cradles, whereas the toothed rim engages the drive gear of electric motor drive that allows the rotation of the converter in both directions through 180 degrees. There is an opening in the middle of the shell, the mouth, for pouring in molten matte, pouring off slag and exhausting gases. With the converter in the working position, the mouth faces up and is located underneath an iron hood which opens up into exhaust flues. Hood edges are cut to suit the external configuration of the converter and fit closely to the mouth to avoid dilution of the gases by air that may be sucked in from the atmosphere. In some converters hoods are provided with a lift-up front wall which improves sealing.

Converters operate on a batch basis, yielding up to 100 tons of blister copper per operation. The outside diameter of a large-size standard converter is 4 m, and its length, 11 m.

Converting Practice

Converting of mattes involves two processing stages. In the first stage, air blast is injected via the tuyeres into the bath of molten matte to stir it vigorously, iron and copper sulphides being oxidized at the surfaces of air bubbles according to reactions (60) and (61) which give off respectively $\Delta H = -940$ kj (225 kcal) and $\Delta H = -777$ kj (186 kcal) of heat.

The cuprous oxide is converted back to sulphide through an exchange interaction with FeS according to reaction (62), with the effect that iron sulphide only is oxidized in the first stage, while copper remains in the form of a sulphide.

Ferrous oxide is slagged by silica (quartz) that is fed to the converter (see reaction 65), the reaction also involving a liberation of heat of $\Delta H = -35$ kj (8.4 kcal). The

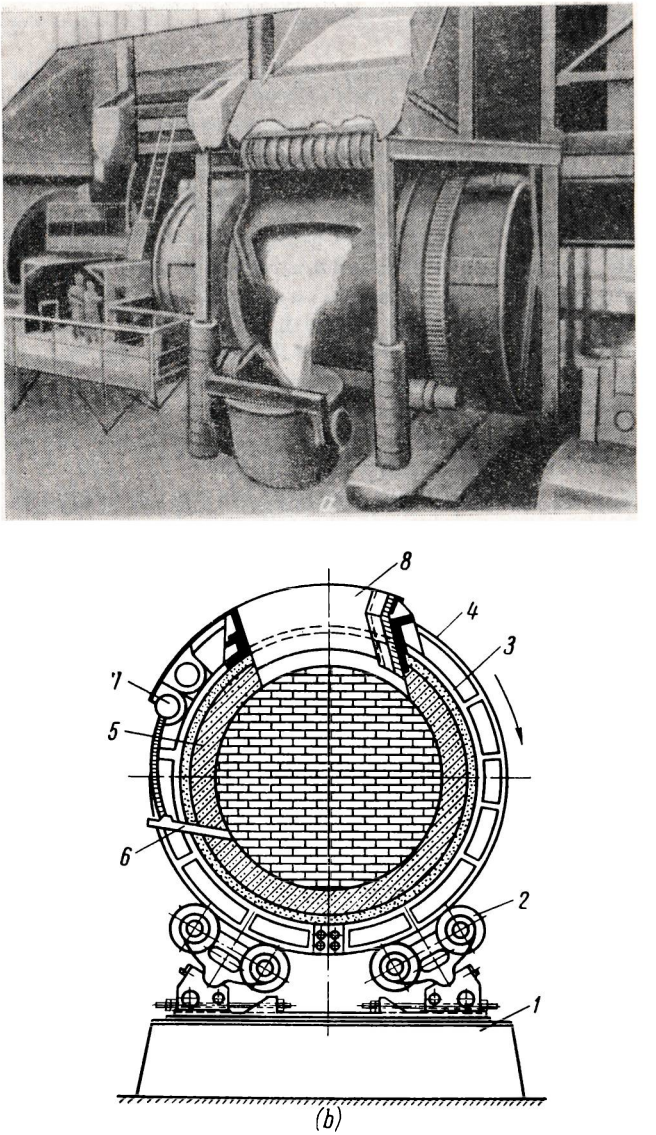

Fig. 34. Modern copper production converter

a—general view; *b*—cross section of converter for matte blowing through
1—foundation; *2*—set of carrying rollers; *3*—shell; *4*—supporting rim; *5*—refractory lining; *6*—tuyere; *7*—air collector; *8*—mouth

oxidation of iron sulphide in the presence of silica (quartz) may be expressed by an overall reaction which is the chief source of heat in a converter

$$2FeS + 3O_2 + SiO_2 \rightarrow Fe_2SiO_4 + 2SO_2; \quad (85)$$

$$\Delta H = -974 \text{ kj (233 kcal)}$$

Should there be a lack of silica (quartz) ferrous iron will oxidize to magnetite

$$6FeO + O_2 \rightarrow 2Fe_3O_4 \quad (86)$$

Magnetite may be reduced by iron sulphide of the matte in the presence of quartz, but should there be too little FeS remaining and should silica (quartz) be in very large lumps the reaction will proceed slowly and fail to go to completion.

A uniform feeding into converters of crushed silica (quartz), 6 to 25 mm in size, and a sufficiently high temperature contribute to reduction of Fe_3O_4, formation of less viscous slags and lowering of mechanical losses of copper. Ferrites that are not reduced during the blow are either dissolved in the slag or pass to it in the form of solid particles, this raising slag viscosity.

Before matte is poured into a converter, the latter should be turned in a manner to position the tuyeres above the melt. The starting temperature of matte is about 1200°C. During the blow it rapidly rises because of an intensive oxidation of sulphides to 1250-1350°C.

Temperature control is imperative, on the one hand, to protect the lining against rapid wear, and, on the other hand, to obtain sufficiently fluid slags. Temperature may be raised by increasing the air supply and adding molten matte, and decreased, by charging solid additives, e.g., ladle skulls, solid matte. Silica (quartz) is fed as soon as blowing through is started.

To avoid excessive splashing, a converter should not be charged to more than 1/3 of its volume. Once a blow through is completed and slag removed, the converter is charged with a fresh portion of starting matte. These operations are repeated until rich melt has been accumulated in a quantity sufficient to pass to the second stage of converting.

Converter slags total about 75 to 90% iron oxides and silica. Practical data from a number of smelters show that in chemical composition converter slags average, %: SiO_2, 17-30; FeO, 50-60; Al_2O_3, 3; Cu, 1.5-2.5.

Less copper is lost in relatively more acid slags because of their lesser magnetite content.

The duration of the first stage of converting is governed by the matte copper content and may vary over a range from 6 to 24 hours.

The second stage of converting takes 2.5 to 3 hours and begins after all the iron is oxidized and slag poured off. Air blown through the white matte oxidizes copper sulphide according to the reaction (61).

The resultant cuprous oxide reacts with the remaining sulphide (reaction 64).

The chemistry of the second stage of converting may be expressed by the equation

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2 \qquad (87)$$

Once a heat is completed, the blister copper is poured off into a ladle which is transported by an overhead crane to an conveyor casting machine where it is poured into moulds. At some smelters, liquid blister copper is fed directly to refining furnaces.

Recovery of copper and noble metals from matte to blister copper (inclusive of converter slag treatment) attains 98.5-99%. The recovery is the higher, the higher the copper content of matte.

Blister copper carries about 1% of impurities (iron, sulphur, oxygen, zinc, nickel, arsenic, antimony and other metals).

First stage converter gases contain 12 to 15% SO_2 and less than 1% of free oxygen, those of the second stage, 15 to 17% SO_2. Converter gases are quite suitable for the manufacture of sulphuric acid or sulphur, but they are not universally utilized to this end because of the batch character of the process.

Dust, carried away by converter gases, consists of solidified droplets of matte, slag and copper, particles of fluxes and volatile oxide impurities. Up to 5% of copper (of the total amount processed) and of noble metals are carried

away with the dust. The greater fraction of these values is contained in the coarser dust which can readily be collected in simple settling chambers or cyclones. The dust is fed back into converters or introduced into the charge of reverberatory furnaces. Finer dust (sublimates) is settled in electric precipitators which are set up downstream of settling chambers. The dust carries concentrated amounts of lead and zinc oxides and rare metals. Sublimates are processed separately.

Tuyeres require cleaning, or punching, at regular intervals when the converter is in operation. Until recently, this arduous work was performed manually by the use of a steel bar and a sledge hammer. Now, up-to-date smelters have introduced mechanized punching devices.

Automatic control of converter operation (blast pressure and draft inside the hood) is the task to be solved in the next few years. Introduction of automatic control will raise SO_2 content still further in the outgoing gases. Automatic turning of a converter to a non-working position in case of blast failure will avoid accidental plugging of tuyeres with matte.

An alternative approach to improve the converting process is to enrich the blast in oxygen. It will reduce blow time and the output of gases, i.e., will raise converter capacity and SO_2 content in the converter gases. Blast oxygenation will also increase the input of heat because of its lesser losses with the outgoing gases. This will allow to charge a greater quantity of silica (quartz) and to obtain slags of higher acidity. For the same reason, operation on oxygenated blast makes it possible to manufacture blister copper directly from concentrates in a converter, by-passing the matte smelting and dispensing with the attendant costs. To this end, the converter is charged with both matte and pelletized copper concentrate, which are blown through, first, to white matte, then to blister copper. It goes without saying that the quantity of concentrates treated in this manner is limited by the additional input of heat from blast oxygenation.

Copper concentrate, conditioned to 8-10% moisture content, is fed to a slowly rotating drum or an inclined pan (Fig. 54). As it rolls over in these apparatus, the concentrate

lumps up and pelletizes to spherical granules up to 20 mm in diameter. The granules, or pellets (which is now the current term), are dried to 2-3% moisture content and charged through the converter's mouth or via the Garr gun. A 2.8-m dia pelletizer produces up to 15 tons of pellets per hour.

Consumption of Air for Blowing Through Matte in a Converter

Determine the consumption of air in the second stage of operation of a 50-ton converter.

The quantity of blister copper obtained by the reaction (87) is

$$\frac{50\,000}{63.54} = 786 \text{ kg-atom}$$

The theoretically necessary amount of oxygen is

$$\frac{786}{2} = 393 \text{ kmole}$$

For a 90% air utilization efficiency, the required amount of oxygen is

$$\frac{393}{90} \cdot 100 = 437 \text{ kmole}$$

The volume of oxygen is

$$437 \cdot 22.4 \approx 9800 \text{ Nm}^3$$

The necessary volume of air is

$$\frac{9800}{21} \cdot 100 \approx 46\,700 \text{ Nm}^3$$

The per minute air flow in a 2-hour blow is

$$\frac{46\,700}{2 \cdot 60} \approx 390 \text{ Nm}^3$$

If the blast is enriched in oxygen to, say, 33%, the required blast consumption will be 29 700 Nm^3, and the per minute blowing rate, 250 Nm^3.

1 mole of O_2 yields 1 mole of SO_2, and, therefore, the quantity of converter gases is approximately equal to the blast flow rate. In consequence, enrichment of blast in

oxygen to 33% reduces the amount of converter gases and the attendant heat losses 1.5 times (with roughly equal heat capacities and same temperatures, heat losses are proportional to gas volumes and fall off somewhat with blow duration).

Treatment of Converter Slags

The yield of converter slags is 2 to 3 times by mass greater than the resulting amount of blister copper. Some 5% copper remain in the slag in the form of solution and as matte or elemental copper inclusions. It calls for additional recovery of this copper.

The present practice of pouring converter slags into reverberatory furnaces or blast furnace settlers is inefficient, as the slag carries large amounts of magnetite which contributes to greater solubility of matte in the slag or dispersion of the matte and formation of colloidal solutions. The effect is greater copper content in the waste slags and greater losses of copper.

A separate processing of converter slags is feasible in a number of ways, inclusive of flotation of crushed slag, settling in electric furnaces, cementation (substitution of iron and cast iron for copper in molten slag) or many other techniques neither of which so far has found preferable industrial application.

Smelting of Blister Copper from Salvage

Salvage and scrap are industrial and household waste, difficult of sorting or differing greatly in chemical composition from standard copper alloys, that are processed to blister copper by techniques allowing a side recovery of other values. Blister copper from these source materials is termed secondary.

Copper waste is graded by size, and the fines are agglomerated in sintering machines, smelting feed being composed of a material 100 to 400 mm in size.

Secondary blister copper is smelted in small blast furnaces. The fuel is coke, its consumption lying between 12 and 17% of the mass of the charge. The fluxes are quartz and limestone,

Copper oxides are readily reducible, and, in consequence, only a slightly reducing atmosphere is required.

Zinc oxides are reduced at the lower levels of the charge column. Zinc and lead vaporize partly, and their vapours are carried away by gases. A considerable amount of these metals passes to slag and blister copper. The fall of dust is 3-4% of the mass of the charge.

The bulk of impurities is removed from the secondary blister copper during the converter blowing through. The required temperature is provided not only by the exothermic oxidation of impurities, but also by the combustion of coke, fed to the converter, at the rate of about 5 kg per ton of copper.

Zinc, lead and tin, oxidized during blowing, pass to slag and dust, the latter's yield being 6-7% of the mass of copper. Dust is processed separately.

Converter slags are cooled, crushed to lumps and proportioned into blast furnace charge. Converter slag zinc content may be as high as 18-20%.

18. Refining of Blister Copper

Blister copper smelted from ore and salvage materials contains 99.2-97.5% of base metal and up to 2.5% impurities, in the first place, iron, sulphur, nickel, bismuth, antimony, gold, silver, selenium, tellurium and dissolved gases.

Many impurities, including gases, affect adversely the mechanical properties of copper, in particular, its plasticity. All impurities, except for the noble metals, have a detrimental effect upon electric conductivity of copper. Blister copper may carry up to 400 g/t Au and up to 3000 g/t Ag. Noble metals are great values and should be extracted in refining.

Grades of commercial copper are described in the USSR by ten grades (Table 13).

There are two general techniques for refining copper, the fire refining and the electrolytic refining.

The former may yield copper of grades M2, M3 and M4. Gold and silver cannot be separated by fire refining. Electrolysis allows production of copper of greater purity and

Table 13

Copper Grades According to Soviet State Standard (GOST) 859-66

Copper grade	Copper, %, min.	Total impurities, %, max.
M00	99.99	0.01
M0	99.95	0.05
M0б	99.97	0.03
Ml	99.90	0.1
Mlp	99.90	0.1
M2	99.70	0.3
M2p	99.70	0.3
M3	99.50	0.5
M3p	99.50	0.5
M4	99.0	1.0

recovery of noble metals. Even though electrolytic refining is more complicated and costly than the fire refining, additional expenses are to a greater degree recouped by side recovery of noble metals.

With the present stringent requirements upon copper purity, it is almost all of blister copper is refined by electrolysis. Refined copper displays much improved properties, and the processing costs can be substantially reduced, if the bulk of impurities is removed by the fire technique, this explaining why fire refining generally precedes electrolytic refining of blister copper.

Fire Refining

Blister copper is refined by the fire technique either in stationary reverberatory-type furnaces (Fig.35) or in rotary cylindrical furnaces, similar in design to a converter. The bath of the stationary furnace is 900 mm deep and holds up to 400 t of molten copper. The furnace is 12-15 m, long and about 5 m, wide.

Refining furnaces are fired with fuel oil, natural gas or pulverized coal, a prerequisite of the fuel being low sulphur since SO_2 of the furnaces gases contaminates copper with sulphur according to the reaction (64) which proceeds to the left.

The furnace bath, laid from silica or special periclase-spinel brick, is enclosed in a shell of cast iron plates and set on pillars. The shell prevents leakage of metal through cracks and faults in the brickwork.

Walls and either a suspended or sprung-and-suspended roof are built of magnesite or magnesite-chrome brick. The walls, faced on the outside with cast iron plates, are provided with working ports and swing-up doors.

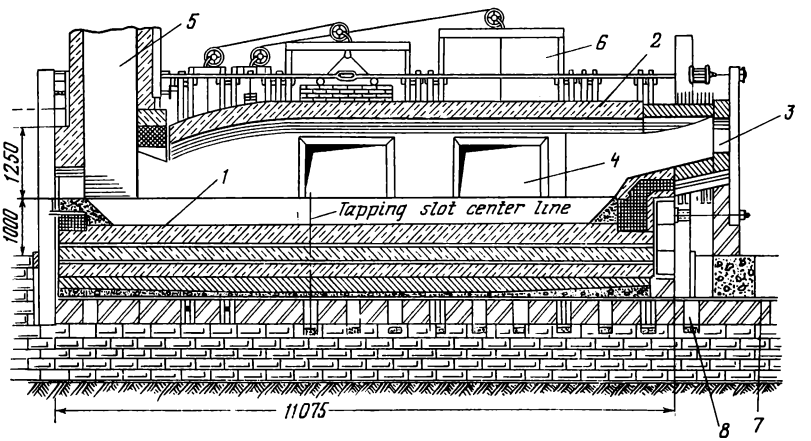

Fig. 35. Copper fire refining furnace

1—hearth; *2*—roof; *3*—burner ports; *4*—working ports; *5*—flue; *6*—doors of working ports; *7*—cast iron plates; *8*—ducts in brickwork

Heating of modern large furnaces is automated: fuel and combustion air are supplied in predetermined proportions. Copper ingots are charged by a mechanical shovel carried by a charging crane (Fig. 36). The shovel has capacity for up to 3.5 tons of copper ingots. Molten copper is poured in with the aid of a crane or from a ladle car of up to 70 tons capacity.

Refining involves the following successive stages: melting, oxidation of impurities and removal of slag, deoxidation (poling) and casting. Overall refining time in operation on solid charge (copper ingots) is 24 hours.

Impurities are oxidized by air which is injected into molten copper through refractory-coated iron pipes 20 to 40 mm

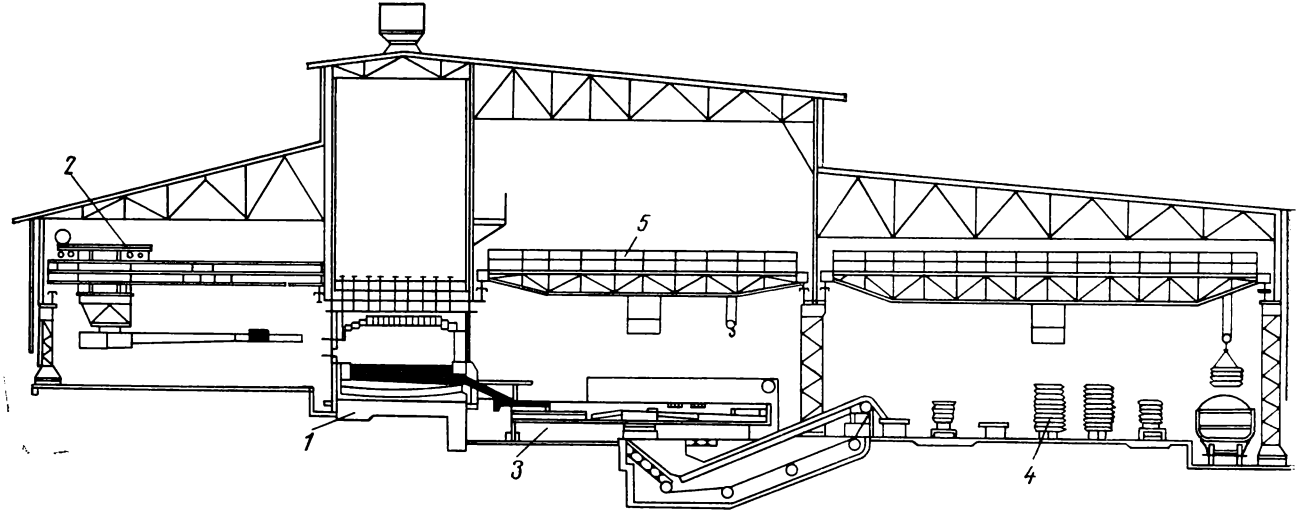

Fig. 36. Copper fire refining plant

1—fire refining furnace; *2*—charging crane with shovel for charging blister copper; *3*—casting machine; *4*—anode; *5*—overhead cranes

in diameter. Oxidation takes place at the surface of air bubbles that float in the molten metal. Oxidized are copper and all impurities, except for the noble metals. The rate of oxidation is proportional to the concentration of metals in the bath, and therefore, it is copper that oxidizes at a highest rate according to reaction

$$4Cu + O_2 \rightarrow 2Cu_2O \qquad (88)$$

Cuprous oxide is soluble in molten copper and rapidly diffuses throughout the bath.

Oxidation of impurities may be described by the general equation

$$Me + Cu_2O = MeO + 2Cu \qquad (89)$$

It is readily apparent from Fig. 3 that such impurities as Al, Si, Mn, Zn, Sn, Fe, Ni, As, Sb, Pb have a greater affinity for oxygen than copper, and, therefore, they all are oxidized by cuprous oxide.

Oxides of impurities are insoluble in molten copper, they float to the surface of molten bath and form with silica of the quartz, that is fed to the furnace, a slag whose skimming and removal from the furnace contributes to the refining effect, since this shifts the equilibrium of oxidation reactions to the right.

For reaction (89), having assumed the activity of copper in the melt to be a constant, we have

$$K_{89} = \frac{a_{MeO}}{a_{Me} \cdot a_{Cu_2O}}$$

A direct relationship between the content of an impurity in a metal and the content of the impurity in the slag becomes readily apparent if it is assumed that the slag is always saturated with Cu_2O. Furthermore, a change of slag tends to decrease a_{MeO}.

Antimony and arsenic can be removed from copper to a greater degree, if soda is added in refining to bind acid oxides Sb_2O_5 and Al_2O_3 into stable sodium antimonates and arsenates.

The order in which impurities oxidize is governed by their affinity for oxygen and their contents in the copper. Less

stable oxides give their oxygen to the more stable ones, e.g.,

$$3FeO + 2Al \rightarrow Al_2O_3 + 3Fe$$

It may roughly be assumed that the order of oxidation of impurities should correspond to that of their decreasing affinity for oxygen, i.e., the impurities should oxidize in the following succession: Al, Si, Mn, Zn, Sn, Fe, Ni, As, Sb, Pb, Bi.

Actually, all the impurities oxidize simultaneously, but at various rates, which are governed not only by their normal affinities for oxygen, but on ratios of their concentrations, slagging abilities, volatilities, oxidation rates and other factors.

Noble metals whose affinities for oxygen are less than that of copper are not removed in fire refining, while bismuth is eliminated but negligibly.

Sulphur, present in copper in the form of dissolved Cu_2S, oxidizes according to the reaction (64) whose equilibrium constant is

$$K_{64} = \frac{p_{SO_2}}{a_{[Cu_2S]} \cdot a^2_{[Cu_2O]}}$$

The concentration of copper may be considered constant and included in the value of K_{64}.

If there is much SO_2 in the furnace gases (sulphurous fuel) activities (concentrations) of Cu_2S and Cu_2O in the metal increase either. Should the SO_2 content be low, the reaction (64) will proceed from left to right, and sulphur will be oxidized and carried away with the gases as SO_2.

The affinities for oxygen of selenium and tellurium are lower than that of sulphur, and, therefore, in oxidizing (fire) refining, these elements remain in copper as Cu_2Se, Cu_2Te and other compounds.

The technique for driving out gases dissolved in molten copper is known as poling down. Green wood (poles or tree trunks) are thrust into the bath of molten copper after slag has been skimmed off. Water vapours and gaseous hydrocarbons that evolve cause vigorous stirring of molten copper and thus contribute to removal of SO_2 and other gases.

After oxidation the copper being refined carries some 12% of Cu_2O, and if a ductile copper is to be obtained, the oxidized melt should be reduced. The reducing agents are wood dry distillation products, i.e., hydrocarbons, for instance,

$$4Cu_2O + CH_4 \rightarrow CO_2 + 2H_2O + 8Cu$$

Reduction involves minimizing air for the combustion of fuel and poling.

Reduction of Cu_2O to a residual content of 0.3 to 0.5% is readily attainable. Deoxidation may be accelerated by injecting fuel oil, pulverized coal or natural gas into molten copper. At some plants, wood has been completely replaced by a mixture of steam and fuel oil or by converted natural gas, conversion being incomplete combustion:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$

Duration of refining is dependent upon the scale of production and the degree of mechanization. Throughput capacity is greatly increased if the charge comprises, wholly or partially, molten blister copper, since melting accounts for roughly 30% of the overall process time and requires additional fuel.

Fire refining slags should be thoroughly removed before copper is deoxidized, otherwise the impurities the slag carries will be reduced from their oxides and pass over to copper.

Slags contain 15 to 40% SiO_2, 5 to 10% Fe in the form of silicates and ferrites, and also oxides of zinc, nickel and other impurities. The slags run 35 to 45% copper, of which 4/5-ths are cuprous oxide, and the balance, unsettled droplets of metal. The yield of slags is 2 to 3% of the mass of copper.

Finished copper is tapped through a vertical tapping slot in the furnace side filled with a stiff mixture of a refractory material and water. When the metal is tapped the refractory material is broken out little by little so the metal can be withdrawn at a required rate. Copper is cast into anodes which are then refined by electrolysis. The rotary casting machine used is a horizontal wheel carrying anode moulds. The wheel revolves slowly, and the cast iron or copper moulds are filled with copper from a pouring ladle which

is set on trestles. When tilted, the ladle fills a mould that is underneath its pouring lip, then the wheel is rotated automatically to bring a next mould underneath the lip and so on. As it moves with the wheel, copper solidifies and is cooled by sprayed water. Finished anodes are immersed for a final cooling into a water tank, then transported to storage. All casting operations are not only mechanized, but many are automated.

Slags from copper refining are smelted by a reducing technique in small blast furnaces to blister copper and waste slag or processed together with mattes in converters.

Fuel consumption in copper refining is 10 to 11% by mass, and a substantial saving on fuel can be effected by installing waste heat boilers downstream of stationary furnaces.

Along with large stationary copper refining furnaces, use is sometimes made of rotary cylindrical refining furnaces of 15-ton capacity, similar in design to converters. These furnaces can readily be accommodated in a common aisle with converters. Rotary furnaces are provided with an opening at one end for the burners, and a working port at the opposite end. Oxidizing air or deoxidizing gas are injected via tuyeres. Blister copper is charged into the furnace through a mouth, which also serves to exhaust gases to a hood, and refined copper is withdrawn through a taphole.

Electrolytic Refining

Copper anodes are placed in a tank with a solution of copper sulphate and sulphuric acid. Suspended parallel to the anodes are thin sheets of pure copper, or starting sheets. The anodes are connected to the positive and the cathodes to the negative poles of a source of direct current.

Anode copper goes into solution according to reaction (13), Table 3, at a potential somewhat more positive than +0.34 V. Contaminating metals of a more negative potential pass into the electrolyte, and those with more positive potentials are settled out at the cell bottom as anode mud. The former include zinc, iron, nickel, tin, arsenic, antimony and bismuth. The behaviour of the latter three differs in that their process of solution runs parallel with hydrolysis with

the effect that these metals present more complicated oxidation-reduction systems

$$2Sb + 3H_2O - 6e^- \rightleftarrows Sb_2O_3 + 6H^+; \quad E^0 = 0.15 \text{ V} \quad (90)$$

$$As + 2H_2O - 3e^- \rightleftarrows HAsO_2 + 3H^+; \quad E^0 = 0.25 \text{ V} \quad (91)$$

$$Bi + H_2O - 3e^- \rightleftarrows BiO^+ + 2H^+; \quad E^0 = 0.32 \text{ V} \quad (92)$$

Impurities more positive than copper are gold, and silver (Table 3) and Cu_2S, Cu_2Se, Cu_2Te and similar compounds of silver in the anodes. They all settle out as anode mud, to which also passes lead (whose cation in the sulfuric solution precipitates as $PbSO_4$) and other insoluble compounds. Cuprous oxide Cu_2O gives a metallic deposit according to reaction (55). An approximate composition of anode mud is as follows, %:

Ag	Au	Cu	Se	Te	S	Pb	As	Sb	Bi
35	2	5	14	6	8	15	3	6	0.3

Compounds of antimony and arsenic are settled out as they accumulate and are oxidized by air oxygen.

It should be noted that some areas of anodes, contaminated by deposits, polarize, this resulting in solution of copper according to system (52).

However, univalent ions are unstable in the solution, and they decompose with the precipitation of metal which passes to mud in accordance with reaction (51).

$$2Cu^+ \rightarrow Cu + Cu^{2+}$$

Polarization can also give rise to an evolution of oxygen (24). Lighter particles of insoluble substances are stirred into suspension by the motion of electrolyte or floated by oxygen bubbles and form a floating or tramp mud which contains up to 50% Sb, 18% As and 0.5% Bi.

Copper ions are reduced from the electrolyte at the cathode according to the same reaction (13), Table 3, which proceeds here in the opposite direction at a potential somewhat less than +0.34 V.

Resultant neutral atoms form copper crystals that stick solidly to the cathode starting sheet. It follows from the data on potentials forming impurities' ions that they can-

not settle out at the cathode together with copper. Zinc, iron, bismuth, arsenic, nickel, antimony and tin are more electronegative, and they remain and accumulate in the electrolyte.

Cathode deposit is contaminated chiefly by entrapped electrolyte and floating mud. To minimize this, part of the electrolyte is periodically removed from baths and purified (regenerated). Sometimes, the electrolyte that is withdrawn is processed separately, and the tanks are replenished with sulphuric acid.

Electric power accounts for a considerable proportion of electrolytic refining costs, which may be expressed with the aid of equation (32) where the quantity of current required to produce one ton of cathode copper can readily be calculated on the basis of the Faraday law. Precipitation of one gram-equivalent of copper, $\frac{63.54}{2} = 31.77$ g, requires 26.8 Ah, and that of one ton of copper

$$(It)_{th} = \frac{1 \cdot 10^6 \cdot 26.8}{31.77} = 0.84 \cdot 10^6 \text{ Ah}$$

where

$$= \text{current intensity, A}$$
$$= \text{time, hours}$$
$$(It)_{th} = \text{theoretical amount of current, Ah}$$

Actually, not all of the current is employed to deposit the copper, and some current is lost because of short-circuits between electrodes, current leakage and discharge of impurities' ions.

Actual consumption of current per ton of cathode copper is

$$(It)_a = \frac{0.84 \cdot 10^6}{K_{ce}} \text{ Ah/t}$$

and the consumption of electric power

$$W = (It)_a V = 0.84 \cdot 10^3 \frac{V}{K_{ce}} \text{ kWh/t}$$

where

K_{ce} = ratio between the theoretical amount of current and that required in practice, or current efficiency

$(It)_a$ = actual amount of current, Ah

The result supplies conclusive evidence that the basis of economical electrolysis is high current efficiency and low voltage drop across the tanks.

The chief constituent of the voltage across a tank according to equation (33) is the voltage drop in the electrolyte IR, since the difference in the potentials of electrodes is rather small, both of them being from copper and placed in the same solution. Practically, the voltage drop ranges from 0.2 to 0.3 V.

Specific electric resistivity of copper sulphate solutions increases with the concentration of $CuSO_4$, but drops sharply if some sulphuric acid is added and the temperature increased.

With the aim of lowering the necessary voltage across tanks, electrolysis is effected in an acidified electrolyte, heated to 60-65°C. The electrolyte usually contains 40-50 g/lit Cu and 150-200 g/lit H_2SO_4.

The distance between electrodes should be at a minimum consistent with prevention of short-circuits and efficient circulation of the electrolyte to make its composition uniform. Spacing of anodes is generally 100 to 120 mm on their centres.

It is good practice to conduct the electrolysis at high current densities, this raising tank capacity, but simultaneously increasing the voltage drop in the electrolyte and the voltage across tanks, and, therefore, the consumption of power due to concentration polarization. Higher polarization is balanced out by intensive circulation of electrolyte, but this may stir up mud, the latter may contaminate cathodes and thus cause greater loss of noble metals.

Optimum density of current is chosen in the range from 180 to 260 A/m^2 on the basis of performance and economical calculations. Current density depends chiefly on the composition of anode copper, latter's content of noble metals and electrolyte circulation rate.

Electrolysis tanks (Fig. 37) are built of reinforced concrete or of standard prefabricated reinforced concrete slabs that are bolted together. The bottom is made of boards. Walls and bottom are protected against attack by electrolyte by sheets of polyvinylchloride (cured at the joints by hot air) or by sheet lead.

Anodes are 40 to 50 mm thick and have a mass of 250 to 320 kg. Starting sheets are electrolytic copper thin sheets obtained by electrolysis in special tanks on stainless steel panels that are oiled to allow ready stripping of the deposit. The stainless panels are removed from the tanks every 24 hours of electrolysis, and two sheets of deposited copper, 0.6 to 0.8 mm thick, are manually stripped off each stainless panel.

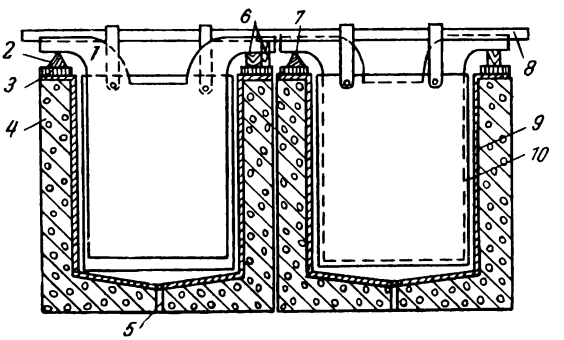

Fig. 37. Reinforced-concrete tanks for electrolysis of copper
1—anode; *2*—copper busbar; *3*—insulation; *4*—tank wall; *5*—hole for discharge of slime; *6*—insulation; *7*—intermediate busbar; *8*—cathodic bar; *9*—vinyl plastic; *10*—cathode

Starting sheets are 30-40 mm wider and longer than the anodes, and their top edges are provided with riveted eyes of the starting sheet material. Copper bars are passed through the eyes to suspend the starting sheets and supply them with current.

Dimensions of the tanks are governed by the size and the number of electrodes. A tank accommodates up to 55 cathodes, by a unit less than the number of anodes. A tank is generally 3.0 to 6.0 m long, by 120-130 mm wider internally than the cathodes, or 1 to 1.1 m, and 1 to 1.3 m deep.

Tanks are set on reinforced concrete piers up to 6 m high, this allowing inspection and repair of their bottoms. Tanks are placed on a glass or diabase insulators to prevent current leakage.

To effect savings on materials, ensure efficient use of shop floorspace and facilitate operation, tanks are generally

arranged in banks of 40-50 or more pieces. Tank electrodes are connected in series, and with this aim the ends of cathode bars are placed upon lugs of anodes of an adjacent tank. Electrical connection of a bank is shown schematically in Fig. 38.

Cathodes and anodes are charged and removed by an overhead crane with the aid of a frame carrying hooks.

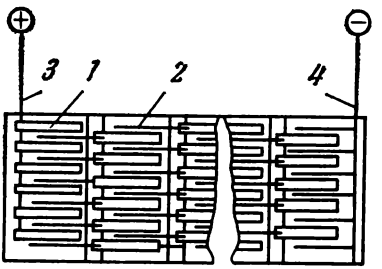

Fig. 38. Electrical connection of tank bank
1—anodes; *2*—cathodes; *3*—anode busbar; *4*—cathode busbar

Anodes are allowed to dissolve for 22-24 days, and their remnants, amounting to about 15% of the initial mass, are remelted and cast to fresh anodes. On the average, cathode build-up takes 6 to 8 days.

Electrolyte is supplied to each tank via a common trunk line from an elevated storage tank, being heated by steam inside the tanks or the pipes as it flows to the electrolysis tanks. Inlet of electrolyte is at one end of the tank, and the outlet, at the opposite end. Intensity of circulation is adjusted by the trial and error method, a complete replacement of the electrolyte taking place generally every 3 or 4 hours.

Loss of heat from the surface of the electrolyte is minimized by covering the tanks with plastic floats, plastic films or organic froths.

Copper plates out at the cathode as a dense deposit. However, the uniformity of its growth is lost with the time, and the cathode surface may be marred by irregularities, bumps and warts. An irregular and loose deposit entraps a large amount of electrolyte and floating slimes, and irregular copper deposits often cause short-circuits between anodes

and cathodes. Small additions of some surfactants to the electrolyte, joiner's glue, gelatin, tannin, pulp production waste, promote greater smoothness and toughness of cathodes and minimize their contamination.

The consumption of these substances is from tenths of a gram to tens of grams per ton of copper. Additions of thiourea and gelatin have been successfully used at some Soviet plants.

On discharge from tanks, cathodes are thoroughly flushed with water, then melted in reverberatory (similar to fire refining) furnaces or in induction furnaces. Cathodes may also be directly shipped to consumers.

Servicing of tanks involves prevention and elimination of short-circuits, provision of as perfect electrical contacts as practical and control of electrolyte temperature, electrolyte circulation and voltage across the tanks.

Up-to-date plants are generally equipped with an automatic control of the electrolyte composition and circulation and the electrolysis conditions.

Direct current is supplied to electrolytic refining plants from motor-generator sets and of late from silicon rectifiers rated for current intensities of up to 13 000 A at 150 to 300 V.

Current efficiency is 94 to 97%, and the consumption of electric power per ton of copper amounts to 200 to 400 kWh.

Purity of electrolytic copper is generally 99.95% (grade MO). At plants where the electrolyte is filtered and additionally purified and the electrolysis conducted at lower current densities, a 99.957 to 99.965% copper is obtained.

After remelting of cathodes, copper is cast into ingots of a special shape intended for wire manufacture. Plasticity and electric conductivity of copper are adversely affected by presence of oxygen and sulphur, whose contents after reverberatory furnace remelting may be as high as 0.04 and 0.0012%, respectively.

Plain induction remelting may yield copper with less than 0.01% of the contaminants, and if a reducing atmosphere is used a copper with $3.0 \cdot 10^{-4}$% O and $1.5 \cdot 10^{-3}$% S may be obtained.

Calculation of an electrolytic refining plant for processing 100 000 tons/year of 99.5% copper anodes is as follows:

The yearly amount of copper requires theoretically

$$\frac{100\,000 \cdot 0.995 \cdot 10^6 \cdot 26.8}{31.77} = 8.30 \cdot 10^{10} \text{ Ah}$$

Assuming a current efficiency of 95%, the amount of electric power actually required will be

$$\frac{8.30}{0.95} \cdot 10^{10} = 8.74 \cdot 10^{10} \text{ Ah}$$

Yearly hours of operation of tanks, exclusive of the time for repairs, will be $350 \cdot 24 = 0.84 \cdot 10^4$ h.

Assuming that the electrolysis will be conducted in a single tank, the required current intensity will be

$$\frac{8.74 \cdot 10^{10}}{0.84 \cdot 10^4} = 10.4 \cdot 10^6 \text{ A}$$

The current density is 250 A/m^2. The total surface area of all the cathodes will then be

$$\frac{10.4 \cdot 10^6}{250} = 4.16 \cdot 10^4 \text{ m}^2$$

The surface area of the working portion of a cathode (starting sheet) is $2 \times 0.88 \times 0.88 = 1.55$ m^2 (on both sides). The number of cathodes required is as follows

$$\frac{4.16 \cdot 10^4}{1.55} = 2.70 \cdot 10^4 \text{ pcs}$$

If the number of cathodes and anodes per tank is assumed to be 30 and 29 respectively, the number of required tanks will be

$$\frac{2.70 \cdot 10^4}{30} = 900 \text{ pcs}$$

Tank voltage is 0.3 V. Losses in the supply circuit and contacts are allowed for by a factor $K = 1.15$. The total voltage of the tank circuit will be

$$900 \cdot 0.3 \cdot 1.15 = 310^* \text{ V}$$

Anodes are spaced 10 cm, and the distance between an outer anode and the tank end is also 10 cm. Tank length will then be

$$\frac{30 \cdot 10 + 2 \cdot 10}{100} = 3.2 \text{ m}$$

The distance from the edge of a cathode to the longitudinal wall of the tank is commonly 5 cm, and, therefore, the tank width will be

$$0.88 + 2 \cdot 0.05 = 0.98 \text{ m}$$

Tanks are generally 1 to 1.1 m deep.

* Total voltage can be increased or reduced to suit the source of electric power by varying the number of cathodes in a tank and the number of tanks.

Purification (Regeneration) of Electrolyte

Regeneration of electrolyte is necessary to avoid build-up of impurities and to remove excess copper. Copper accumulates in the electrolyte through partial chemical solution involving participation of air oxygen

$$2Cu + O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + 2H_2O \quad (93)$$

In addition, anodes contain some cuprous oxide which is soluble in sulphuric acid (55).

Copper passes into the electrolyte in an amount 0.5 to 1% above that deposited at the cathodes, and as its percentage goes up it may begin to crystallize, particularly, at the surface of the anodes.

If impurities' content is low and excess copper is only to be extracted, the electrolyte is processed by electrolysis in standard tanks, but furnished with insoluble lead anodes. Copper of the electrolyte plates out at the cathodes in the process, oxygen evolves at the lead anodes, while some free sulphuric acid forms in the solution. Once copper is partially extracted, the electrolyte may be returned to the circulation system.

Tank voltage in the electrolysis with insoluble anodes is about 2.5 V. Power consumption in the tanks is approximately by a factor of 10 greater than in the electrolysis with soluble anodes.

The electrolysis technique offers no advantages when the removal of not only copper, but of impurities as well is aimed at. The impurities can be removed only after all of copper has been deposited by electrolysis. Copper deposits from weak solutions tend to be loose and are contaminated by impurities.

If that is the case, the electrolyte that has been "bled" out of the circulation system is neutralized by copper scale or plain copper, the electrolyte being heated and blown through with air to speed up the solution of copper. Hot solution is allowed to flow to special tanks where sulphate crystals $CuSO_4 \cdot 5H_2O$ precipitate. The mother liquor is evaporated and allowed to crystallize again and so yield an additional amount of copper sulphate (blue vitriol). Vacuum apparatus are used at some plants for evaporation and crystallization.

Crystallization, precipitation of a dissolved substance as solid crystals, is carried out from supersaturated solutions the concentration of which after cooling is supersaturated with respect to the final temperature. A solution is supersaturated by either cooling or vaporizing a part of the solvent. In both cases crystallization starts with formation of nuclei, or minute primary particles of a solid, which then grow by fixing on its surface ions of the solute in a geometrically regular pattern (crystalline lattice) that is characteristic of the substance.

Size of crystals is governed by the rate of formation of nuclei and their growth. If the nuclei tend to form rapidly, but grow at a slow rate, the crystals are small. If the speeds are reversed, the resulting crystals are large.

Formation of nuclei is promoted by a rapid supersaturation of the solution, i.e., through sharp cooling and contact with a large surface of an insoluble solid substance. In the case in question, the hot copper sulphate solution is transferred for cooling into a tank with strips of sheet lead suspended to its edges. Nuclei tend to originate at these strips and grow to large crystals.

The crystalline lattice entraps molecules of the solvent (water), and, therefore, the chemical composition of copper sulphate (blue vitriol) is given by the formula $CuSO_4 \cdot 5H_2O$. Impurities concentrate in the mother liquor remaining after crystals are removed.

The above crystallization technique is far from being perfect, as it requires large-size tanks and is slow. There are many designs of more efficient crystallizers. Vacuum crystallizers, discussed below (see p. 382), are particularly efficient and economical.

Use is often made of a combined regeneration technique in which a part of the electrolyte is denuded of copper by electrolysis and recycled. The balance of the electrolyte is processed to copper sulphate, while the final mother liquor is treated by electrolysis to recover the bulk of copper, then vaporized to produce nickel sulphate (nickel vitriol), should nickel accumulate in the electrolyte.

Anode Mud Processing

Anode mud precipitates at the tank bottom, but some of it remains in the electrolyte as a suspension (floating slime). Anode mud is discharged as the tanks are cleaned at regular intervals and processed.

The chief values the anode mud carries are noble metals, selenium and tellurium, which are removed after copper is extracted by leaching with hot diluted sulphuric acid and by blowing through with air. The insoluble bottoms are roasted with soda, selenium and tellurium forming in the

process water-soluble sodium selenites and tellurites Na_2SeO_3 and Na_2TeO_3. Some selenium also evaporates as SeO_2 which is removed from gases by dust collectors.

The sintered product is leached by water, and selenium and tellurium are recovered from resulting solutions. Leaching residues are melted with soda and oxidizers to an alloy of gold and silver, the dore metal, which is forwarded to gold refining plants for cleaning of impurities and separation into gold and silver (Para. 34).

19. Hydrometallurgy of Copper

Besides pyrometallurgy, copper may be manufactured by hydrometallurgical techniques which although less extensively used hold great prospects. Hydrometallurgy in its widest sense consists in leaching of ores by various solvents and subsequent reduction of copper from solution either by cementation (direct substitution) or electrolysis. As a first step in the concentration of copper and its separation from impurities use is now made of ion exchange and extraction techniques.

Choice of leaching conditions may be facilitated by thermodynamical calculations of the possibility of the chemical reactions involved which are feasible if their equilibrium constants are much greater than unity. The logic of such an evaluation is easy to understand: the numerator of the expression for K (equilibrium constant) is a product of the concentrations (activities) of resultants, and the denominator, that of the concentrations of starting substances. Thermodynamical data on minerals are often lacking in technical literature or are unreliable. For this reason, use can be made in approximate calculations of constants of similar chemical compounds.

Mineral malachite $CuCO_3 \cdot Cu(OH)_2$ corresponds in composition to copper carbonate $Cu_2(OH)_2CO_3$ whose product of solubility is $Sp = 1.7 \cdot 10^{-34}$*. The reaction of malachite with sulphuric acid is

$$Cu_2(OH)_2CO_3 + 2H_2SO_4 \rightleftarrows CuSO_4 + 3H_2O + CO_2 \quad (94)$$

* Here and below all standard values are from the Handbook of Analytical Chemistry by Yu. Lourié, Moscow, 1971.

Ion SO_4^{2-} plays no part in the reaction as H_2SO_4 and $CuSO_4$ are strong electrolytes and, therefore, the concentration of SO_4^{2-} does not vary in the course of the reaction, whereas H_2O and CO_2 give H_2CO_3, the critical solubility of which in water at 20°C is $3.8 \cdot 10^{-2}$ milligrams/litre.

To calculate the reaction, let us write it in ionic form and subdivide it into steps

$$Cu_2(OH)_2CO_3 + 4H^+ \rightleftarrows 2Cu^{2+} + 2H_2O + H_2CO_3$$

1*. $Cu_2(OH)_2CO_3 \rightleftarrows 2Cu^{2+} + 2OH^- + CO_3^{2-}$;

$$K_1 = a^2_{Cu^{2+}} \cdot a^2_{OH^-} \cdot a_{CO_3^{2-}} = SP_{Cu_2(OH)_2CO_3}$$

2**. $2H^+ + 2OH^- \rightleftarrows 2H_2O$;

$$K_2 = \frac{a^2_{H_2O}}{a^2_{H^+} + a^2_{OH^-}} = \frac{1}{K_w^2}$$

3. $H^+ + CO_3^{2-} \rightleftarrows HCO_3^-$; $\quad K_3 = \dfrac{a_{HCO_3^-}}{a_{H^+} \cdot a_{CO_3^-}} = \dfrac{1}{K_{HCO_3^-}}$

4. $HCO_3^- + H^+ \rightleftarrows H_2CO_3$; $\quad K_4 = \dfrac{a_{H_2CO_3}}{a_{HCO_3^-} \cdot a_{H^+}} = \dfrac{1}{K_{H_2CO_3}}$

$$K = K_1 \cdot K_2 \cdot K_3 \cdot K_4 \ldots = \frac{SP_{Cu_2(OH)_2CO_3}}{K_{2w} \cdot K_{HCO_3^-} \cdot K_{H_2CO_3}}$$

Thus, it has been possible to express the constant of equilibrium of the reaction through the available thermodynamic data that are written as negative logarithms for better convenience

$$-\log K = -(\log SP_{Cu_2(OH)_2CO_3} - 2\log K_w - \log K_{HCO_3^-} - \log K_{H_2CO_3}) = (p \cdot SP_{Cu_2(OH)_2CO_3} - 2pK_w - pK_{HCO_3^-} - pK_{H_2CO_3}) = 33.78 - 28 - 10.32 - 6.35 = -10.89$$

$$K = 7.8 \cdot 10^{10}$$

Having expressed K through concentrations, we can calculate, for example, the acidity of a solution, containing 63.54 g/lit of 1 g-ion Cu^{2+}, in equilibrium with malachite (assuming activities equal to

---

* A unity should be written in the numerator, since the constancy of $Cu_2(OH)_2CO_3$ concentration has been accounted for by K_1.

** Concentration of water in aqueous solutions is assumed to be constant and is included in K_2 which will be a reciprocal of the square of ionic product of water.

unity for the sake of simplicity)

$$K = 10^{10.89} = \frac{[Cu^{2+}]^2 \cdot [H_2CO_3]}{[H^+]^4} = \frac{3.8 \cdot 10^{-2}}{[H^+]^4};$$

$$-\log [H^+] \approx pH = -\frac{1}{4}(-2 + \log 3.8 - 10.89) = 3.08$$

It follows from the calculation that leaching of malachite is feasible and requires a small equilibrium acidity. A different result is obtained in the calculation of covellite CuS leaching

$$\begin{aligned} CuS + H_2SO_4 &\rightleftarrows CuSO_4 + H_2S \\ CuS + 2H^+ &\rightleftarrows Cu^{2+} + H_2S \end{aligned} \qquad (95)$$

(a) $CuS \rightleftarrows Cu^{2+} + S^{2-}$; $K_1 = Sp_{CuS}$; $pSp = 35.20$

(b) $H^+ + S^{2-} \rightleftarrows HS^-$; $K_2 = \frac{1}{K_{HS^-}}$; $pK_{HS^-} = 12.89$

(c) $H^+ + HS^- \rightleftarrows H_2S$; $K_3 = \frac{1}{K_{H_2S}}$; $pK_{H_2S} = 6.99$

$K = K_1 \cdot K_2 \cdot K_3$; $pK = 35.20 - 12.89 - 6.99 = 15.32$;

$K = 10^{-15.32}$

The reaction is unfeasible, and that for chalcocite is even less probable as $pSp = 47.6$.

It should be noted that data on solubility products are more reliable than Δz values, obtained by extrapolation of experiments at high temperatures, and, therefore, in relation to hydrometallurgical reactions this calculation procedure is more accurate than that involving equation (2).

Leaching of sulphides by trivalent iron salts may be exemplified by the reaction involving covellite

$$CuS + 2Fe^{3+} \rightleftarrows Cu^{2+} + 2Fe^{2+} + S^0 \qquad (96)$$

1. $CuS \rightleftarrows Cu^{2+} + S^{2-}$; $K_1 = Sp_{CuS}$; $pSp = 35.20$
2. Oxidizer: $2Fe^{3+} + 2\bar{e} \rightleftarrows 2Fe^{2+}$; $E^0 = 0.77$ V
   Reducer: $S^{2-} - 2\bar{e} \rightleftarrows S^0$; $E^0 = -0.48$ V

$$pK_2 = \frac{-0.48 - 0.77}{0.06} \cdot 2 = -41.6$$

$$pK = pK_1 + pK_2 = 35.2 - 41.6 = -6.4; \quad K = 2.5 \cdot 10^6$$

which indicates that the reaction is feasible.

In a compound similar to chalcocite trivalent iron oxidizes both copper and sulphur

$$Cu_2S + 4Fe^{3+} \rightleftarrows 2Cu^{2+} = 4Fe^{2+} + S^0 \qquad (97)$$

1. $Cu_2S \rightleftarrows 2Cu^+ + S^{2-}$; $K_1 = SP_{Cu_2S}$; $pSP_{Cu_2S} = 47.6$
2. Oxidizer: $4Fe^{3+} + 4\bar{e} \rightleftarrows 4Fe^{2+}$; $E^0 = 0.77$ V
   Reducers:
   (a) $2Cu^+ - 2\bar{e} \rightleftarrows 2Cu^{2+}$; $E^0 = 0.15$ V
   (b) $S^{2-} - 2\bar{e} \rightleftarrows S^0$; $E^0 = -0.48$ V

$$pK_{2a} = \frac{0.15 - 0.77}{0.06} \cdot 2 = -20.6;$$

$$pK_{2b} = \frac{-0.48 - 0.77}{0.06} \cdot 2 = -41.6;$$

$$pK = pSP_{Cu_2S} + pK_{2a} + pK_{2b} = 47.6 - 20.6 - 41.6 = -14.6$$

$K_{97} = 10^{14.6}$, which indicates that the reaction is feasible.

There are no reliable thermodynamical data for bornite and chalcopyrite. However, it is known from experiments that these minerals are insoluble in sulphuric acid, but tend to go slowly in solution in the presence of salts of trivalent iron.

From mineralogical data, chalcopyrite may be visualized as $CuS \cdot FeS$ or $Cu_2S \cdot FeS \cdot FeS_2$.

The structure of bornite is even more complicated, being similar to solid solutions of $CuFeS_2$ and $2Cu_2S$, as some facts tend to indicate.

Thermodynamical data for these minerals are very questionable, but even without calculations it is reasonable to expect that they will interact with ferrous oxide salts and acids more vigorously than the simpler copper sulphides.

The chemistry of oxidation of chalcopyrite and bornite in solutions of trivalent iron salts may be tentatively described by the following equations

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0$$

$$Cu_5FeS_4 + 12Fe^{3+} \rightarrow 5Cu^{2+} + 13Fe^{2+} + 4S^0$$

There are no data on chrysocolla either, which is known from experiments to be slowly soluble in acids, probably, because of formation of a surface film of silicic acid

$$CuSiO_3 \cdot 2H_2O + 2H^+ + (n-2)H_2O \rightarrow Cu^{2+} + H_2SiO_3 \cdot nH_2O \qquad (98)$$

The rate of leaching is another precondition for latter's feasibility. Some of the thermodynamically feasible reactions are so slow in aqueous solutions that their commercial use is out of question.

Interaction of a solute with a solid particle is a multistage process which begins with the supply of a reagent to the particles' surface by diffusion, there being many obstacles such as, the resistance of layers of foreign substances, surrounding the mineral and negatiated by penetration through pores and cracks. The reagent is next adsorbed on the surface of the mineral, interacts with it, the resultant product is desorbed and by the same complicated path returns to the solution. In this succession of reactions, the rate of the process as a whole is determined, or controlled, by the slowest stage which is generally diffusion, but may also be a chemical reaction.

Diffusion may often be speeded up by stirring which causes the process to shift from the molecular (27) to the convective region. Owing to greater speed of flow of a fluid with relation to a surface of a solid, the δ value drops (27), but only to a predetermined limit beyond which intensification fo stirring fails to accelerate leaching.

Heating promotes diffusion because of an increase of D (27), the action being generally describable by a temperature factor which indicates how many times leaching is speeded up for a 10°C increase in temperature.

$$K_t = \frac{K_{t_0+10}}{K_{t_0}} \approx 1.3 \text{ to } 1.5$$

When the rate of the chemical reaction is low, or, as it is said, the rate is controlled by its kinetics, we have

$$K_t = 2 \text{ to } 3$$

Heating is more advantageous here, whereas intensified stirring is ineffective.

Reduction in size of the solid material is frequently very effective, since it not only increases the aggregate surface area of particles, but removes all foreign coats. However, overgrinding is very costly and may, moreover, render difficult the separation of the insoluble residue by thickening or filtering.

Leaching Techniques

Leaching may be carried out by underground method (on ore in place), in heaps, by percolation and by agitation (stirring) of pulps. *Underground leaching* may be either natural or artificial (organized). The former takes place when soil water penetrates abandoned mines where some rocks lean in copper remain as their mining was unprofitable.

In the process, pyrite is oxidized by air oxygen in solution in water according to the reaction

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4H^+ + 8SO_4^{2-} \qquad (99)$$

It is of interest to calculate the equilibrium conditions of the above reaction by two procedures, by the use, first, of equation (2), and, second, of oxidation-reduction potentials.

$$\Delta Z^* = 8\Delta Z_{SO_4^{2-}} + 4\Delta Z_{Fe^{3+}} - 4\Delta Z_{FeS_2} - 2\Delta Z_{H_2O}$$

$$8\,(-177.34) + 4\,(-2.53) - 4\,(-39.84) - 2\,(-56.7) = -1156.1 \text{ kcal}$$

According to the second procedure, having divided the reaction into steps, we find

1. $4FeS_2 \rightleftarrows 4Fe^{2+} + 4S_2^{2-}$; $K_1 = Sp^4_{FeS_2}$; $pK_1 = 4 \cdot 30.2 = 120.8$
2. Oxidizer:

$$15O_2 + 60H^+ + 60e^- \rightleftarrows 30H_2O;\ E^0 = 1.23 \text{ V}$$

Reducers:

(a) $4Fe^{2+} - 4e^- \rightleftarrows 4Fe^{3+}$; $E^0 = 0.77$ V

(b) $4S_2^{2-} - 8e^- \rightleftarrows 8S^0$; $E^0 = -0.48$ V

(c) $8S^0 + 32H_2O - 48e^- \rightleftarrows 8SO_4^{2-} + 64H^+$; $E^0 = 0.36$ V

$$pK_2 = \frac{(0.77 - 1.23)\,4 + (-0.48 - 1.23)\,8 + (0.36 - 1.23)\,48}{0.06} = -936$$

$$pK = pK_1 + pK_2 = 120 \cdot 8 - 936 = -815.2$$

Hence,

$$\Delta Z = -RT \ln K = -1.987 \cdot 303 \cdot 2.30 \log K = 1386\ pK = 1129 \text{ kcal}$$

---

* Isobaric potential values in aqueous solutions have been taken from V. Lathimere, Oxidation State of Elements and Their Potentials in Aqueous Solutions, in Russian, Moscow, Foreign Literature Publishing House, 1954.

The difference in the results amounts to about 2.5% because of a discrepancy of starting values.

The former procedure is simpler as to arithmetics, but the latter allows a better judgement on the probable oxidation mechanism. In particular, it indicates that acids in mine water are not from hydrolysis of iron salts, but from oxidation of pyrite sulphur.

It was discovered recently that oxidation of iron and sulphur may be promoted (99) by some bacteria whose habitat is soil and water of excavations from mining of sulphide ores or coals. Brief information on some of these is given below.

Name of bacteria	Activity	Optimum living conditions	
		t° C	pH
Thiobacillus thiooxidans	Oxidize sulphur and sulphides	28-32	2
Thiobacillus ferrooxidans (Fig. 39)	Oxidize Fe^{2+} and sulphur ions	—	2.5-2.8
Ferrobacillus ferrooxidans	Same	15-20	3.5
Ferrobacillus sulphooxidans	Oxidize Fe^{2+} and sulphur	32	2.8

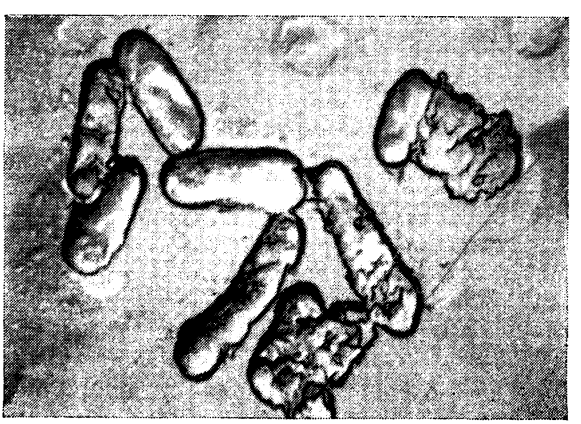

Fig. 39. Bacteria Thiobacillus ferrooxidans, X 40,000

If in sufficient quantity, bacteria greatly speed up reaction (99), and resultant acid solutions of trivalent iron leach copper according to reactions (94 through 97) and also minerals of other metals.

In the artificial (organized) leaching, solutions with the same reagents, H_2SO_4 and $Fe_2(SO_4)_3$, often carrying cultures of said bacteria, are pumped into the body of lean ores through holes of various depths that have been drilled with due regard to the shape of the ore body and effectiveness of circulation. They are equipped with perforated pipes of stainless steel or plastics. If rock permeability is poor, additional holes are drilled to allow hydraulic or other type of mellowing. Large ore bodies are loosened by blasting, sometimes by that of nuclear devices. Liquor inlets and outlets are changed at regular intervals to provide time for the oxidation and development of bacteria.

Leaching in Refuse Ore and Heaps

Before an ore with 0.3-2% Cu is piled into heaps, it is crushed to 10-30 mm. A heap shaped as a truncated pyramid 10 to 30 m high may hold up to 600 000 tons of ore. The base for the heap is a water-tight plot, covered with clay, asphalt or polyethylene film. The heap is showered with water by sprayers or pools of water, 30 to 60 cm, deep, are arranged on tops of heaps. In some instances, vertical perforated pipes are inserted into heaps. Run-off from heaps is collected by systems of ditches, runners or pipes and returned to showering, while some of the liquor is withdrawn and processed for recovery of metals.

Characteristic of leaching of old refuse ore is low copper content (0.1 to 0.3%), the material generally being ore dressing tailings. Average capacity of refuse ore dumps is 10^6 to 10^9 tons. Essential to successful heap leaching are suitable site topography (hollows) and natural water-tightness of the underlying soil.

Heaps and refuse ore dupms are provided with truck roads or railway tracks, rain ditches to prevent flooding. Side surfaces are protected against spreading by planting grass.

An approximate chemical composition of liquors from heap and underground leaching, gram/litre, is given below

Cu	Fe	Zn	H_2SO_4	Solid particles
0.3-3	0.1-8	0.1-0.5	0.5	Up to 20

Combining of heap and underground leaching may activate bacteria as liquors percolate through the heaps and thus raise the concentration of copper 2 or 3 times.

Every year, leaching of below grade ores yields some 10 000 tons of copper which costs one half of that smelted from grade ore.

Leaching by Percolation

Percolation is used to extract copper from mechanically strong, porous oxidized ores (0.6 to 2% Cu) which are first crushed and sized to obtain a fraction of 4 to 10 mm, adequately permeable to solutions when heaped in layers 3 to 4 m thick. Fines are sometimes humidified and pelletized (Fig. 54*a*) or leached separately in stirred tanks.

Percolators are basins of concrete, infrequently of wood, respectively either prismatic or cylindrical, having capacity of 5000 to 10 000 tons of ore, tentatively, 50 m long, 30 m wide, 5 m deep. Inside surfaces are protected against attack of acid liquors by asphalt, resins, acid-resistant concrete, sometimes lead. A grid of wooden squared beams or planks, spaced 15 to 20 cm apart, is placed on the percolator's bottom then covered with synthetic cloth, bast or coconut fibre mats.

Leaching liquor is supplied from the top, downward or gravity percolation, or from below, upward percolation. Time of contact of liquor with ore may be 10 to 15 days. In small-scale manufactures, ore is leached in batches by recycled liquor, and tailings are washed by water, whereas in larger installations use is made of a countercurrent technique which involves percolation by solutions of a gradually growing content of reagents. The process is so organized that, for example, one percolator of a bank is being excavated, another one is being charged with ore and liquor is

being circulated countercurrently through the remaining vats, i.e., a liquor high in copper leaches a newly charged ore, whereas a fresh solution is used to treat an almost completely leached ore.

Rate of percolation is evaluated in terms of litres of liquor passing in one hour through a column of ore one square metre in cross section. Adequate and good rates are 20-60 and 80-90 litre/m^2, respectively. Heating of liquors and addition of flocculators promotes faster percolation and improves extraction of copper, but costs very much.

Ore is charged and excavated by grab-bucket cranes, while tailings are dumped by means of belt conveyors or hydraulic techniques as pulp. The latter method should be avoided if possible because of pollution hazard.

Copper is recovered by about 70 to 90% its losses being caused by a difficult penetration of liquor inside ore lumps. However, running costs in large-scale installations are quite low, chiefly because no fine grinding or filtering of solutions is required. Percolation is considered an obsolete technique, but it is still in use.

Agitation Leaching

Oxidized ores unsuitable for percolation because of size and permeability to liquors are leached by agitation in vats equipped with stirrers. Ore, ground generally to less than 1 mm, is repulped by a sulphuric acid liquor, and the pulp (liquid to solids ratio of 1.5 to 4) is stirred in pneumatic or mechanical tanks, usually without heating, for 2 to 6 hours. Tailings are separated by settling in thickeners, washed by decantation, repulped again by water and settled out again, then filtered and washed on a filter. Resulting solutions are less and less rich in copper, i.e., from 40 to 5 gram/litre. Richer solutions are processed by electrolysis, and leaner ones are recirculated.

Vats for stirring pulp, ranging in capacities from 20 to 200 m^3, are built of alloy steel, wood or concrete, protected against sulphuric acid by lead, asphalt, rubber, acid-resistant brick or ceramic tiles.

Pulp is generally stirred by air or steam as they cost less than mechanical means.

A pneumatic agitator (Fig. 76), also known as a Pachuka tank*, is a high cylindrical vat with a conical bottom, 3 to 4 m in diameter, 8 to 9 m high, up to 200 m^3 in capacity, fitted with a pipe, open at both ends, placed in the axis of the vat and supported by cross bars. Compressed air at about 196.2 kN/m^2 (2 abs. atm.) is supplied to the bottom end of the pipe. Pulp is run to the vat from the top and continuously withdrawn along a runner at a level somewhat lower than the top of the central pipe. As air bubbles through the pulp, it raises latter's level inside the pipe and causes it to flow continuously over into the tank. For the same reason, pulp is sucked into the pipe at the bottom. Thus, the pulp is caused to circulate inside the tank to ensure effective stirring. Tank bottom is conical, and, therefore the solid particles that settle out collect underneath the bottom hole of the pipe and are re-agitated.

Precipitation of Copper by Cementation

The precipitant in the reaction (34) is iron chips, wire waste and sheet iron of used food cans which has been stripped of tin by hot NaOH liquors (Fig. 40). Varnished sheet iron of food cans is fired to remove and burn organic matter, then crushed and crumpled.

Standard cementation equipment are straight-line or zig-zag wood or concrete troughs tens of metres long, up to 2 m wide and up to 1.5 m deep. Scrap is charged by cranes or electromagnet lift trucks onto wooden grids. When stirred by the same mechanisms, the precipitate falls through latter's openings, is flushed by water and discharged through pipes. Liquor is supplied under pressure via a perforated pipe placed on trough bottom, and as it trickles down it flushes precipitated copper off the scrap surface.

Besides troughs, which require much floorspace, use is made of rotary drum and of tanks, whereas scrap may be replaced by sponge iron obtained by reduction of rich iron ores and scale.

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* So named after a Mexican village Pachuka where it has been put in use for the first time.

Conical cementators are more perfect in design. Liquor is supplied via a downward-oriented cone apex, and sponge iron, through the top. Large particles of iron that are in suspension at the bottom interact with the more concentrated solution, whereas finer particles float at the top and

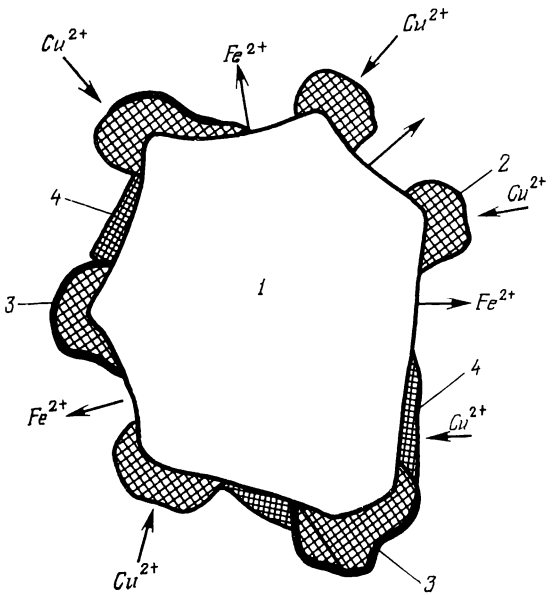

Fig. 40. Cementation of copper by iron

1—iron particle; *2*—points where copper settles out; *3*—surface contamination of copper deposit; *4*—spreading of deposit over new areas of surface of iron

react with a weaker liquor. Pulp is filtered or thickened, and filtrates are returned to leaching after their divalent iron has been oxidized by air.

Besides oxidation, it is also essential to remove excess Fe^{3+} which accumulates at each cycle. Divalent iron is oxidized by air oxygen in artificial pools where liquors are directed after cementation.

In an acid medium, divalent iron is oxidized by air oxygen according to the reaction

$$\left.\begin{array}{ll} 1. & O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O; \quad E^0 = 1.23 \text{ V} \\ 2. & 4Fe^{2+} - 4e^- \rightleftarrows 4Fe^{3+}; \quad E^0 = 0.77 \text{ V} \end{array}\right\}$$

$$pK = \frac{0.77 - 1.23}{0.06} \cdot 4 = -30.7$$

$$4Fe^{2+} + O_2 + 4H^+ \rightleftarrows Fe^{3+} + 2H_2O; \quad K = 5 \cdot 10^{30} \quad (100)$$

To precipitate excess trivalent iron, lime is added as it lowers acidity and promotes hydrolysis which results in settling of basic salts such as $Fe(OH)_nSO_m$ or hydroxide of trivalent iron

$$1. \quad Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+$$

$$2. \quad FeOH^{2+} + H_2O \rightarrow Fe(OH)_2^+ + H^+$$

$$3. \quad Fe(OH)_2^+ + H_2O \rightarrow Fe(OH)_3 + H^+$$

$$Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^+ \quad (101)$$

$$K_{101} = \frac{a_{H^+}^3}{a_{Fe^{3+}}} = \frac{K_w^3}{S p_{Fe(OH)_3}}; \quad pK_{101} = 3 \cdot 14 - 37.5 = 4.5;$$

$$K_{101} = 3.1 \cdot 10^{-5}$$

This allows to calculate pH at the beginning of hydrolysis

$$a_{H^+} = \sqrt[3]{a_{Fe^{3+}} \cdot K_{101}}$$

Having assumed $a_{Fe^{3+}} = 1$ gram-ion/litre, we obtain pH of 1.5, whereas for $a_{Fe^{3+}} = 0.01$ milligram/litre, pH = = 2.2.

Recovery of copper by settling in troughs ranges from 90 to 97% for flow rates of 0.5 to 3 m/min and capacities from 5 to 50 kg/m³ per 24 hours. Consumption of iron is a 1.5 to 2.5 multiple of copper's mass. Conical cementators provide a recovery by 2 to 3% higher than the above values.

Processing of Cement Copper

Cement copper precipitates contain from 30 to 90% Cu. Depending on its quality, it is processed in either of three ways: smelted together with copper charges in reverberatory furnaces, briquetted and charged into converters; or remel-

ted and refined in a separate process. Some plants process cement copper in autoclaves to powder of 99.95% purity, suitable for briquetting and subsequent remelting in protective or reducing atmosphere to oxygen-free copper.

Copper powder may be pressed to form articles of required shape with less waste as well as strips, pipes, shaped rolled stock and parts of machines. If the powder is contaminated, it is rolled to anodes for electrolytic refining.

In the above technique, cement copper is leached at a temperature of 80-90°C by recycled liquor from autoclaves which contains 125 gram/litre of H_2SO_4 and $(NH_4)_2SO_4$ each. When oxygenated air is injected into the pulp, copper dissolves according to reaction (36).

After filtering, solutions with 100 gram/litre Cu and impurities and a pH of about 2 are directed to titanium-lined autoclaves. Not more than 1% copper is lost with the insoluble residue.

Some 80 to 90% of copper settles out in autoclaves in 2 or 3 hours according to reaction (40) at a temperature of 130-140°C and hydrogen pressure of 25 abs. atm.

Impurities such as iron, nickel, zinc remain in solution if their quantities are small, and liquor is purified by removing impurities through ion-exchange sorption on ionites before liquor is fed to autoclaves.

Once separated, powder is washed, dried and calcinated in a hydrogen atmosphere at 600 to 700°C.

Cement copper may be processed by the use of ammonia and ammonium carbonate according to reactions

$$2Cu + 8NH_3 + O_2 + 4H_2O \rightarrow 2Cu(NH_3)_4^{2+} + 4OH^- \quad (102)$$

$$2Cu + O_2 + 8NH_4^+ \rightarrow 2Cu(NH_3)_4^{2+} + 2H_2O + 4H^+ \quad (103)$$

It may be of interest to compare equilibrium constants of reactions (102) and (103) at a constant pressure of oxygen

$$K_{102} = \frac{a^4_{OH^-} \cdot a^2_{Cu(NH_3)^{2+}}}{a^8_{NH_3}}$$

The reaction may be broken down to the steps below

$$\left.\begin{array}{l} 1.\ 2Cu - 4\bar{e} \rightleftarrows 2Cu^{2+};\quad E^0 = 0.34\ V \\ O_2 + 2H_2O + 4\bar{e} \rightleftarrows 4OH^-;\quad E^0 = 0.40\ V \end{array}\right\} pK_{ox/red} =$$

$$= \frac{0.34 - 0.40}{0.06} \cdot 4 = -4$$

2. $2Cu^{2+} + 8NH_3 \rightleftarrows 2Cu(NH_3)_4^{2+}$; $pK_2 = -2pK_{Cu(NH_3)_4^{2+}} = -24.06$;

$$pK = pK_1 + pK_2 = -4 - 24.06 = -28.06;$$

$$K_{102} = 1.1 \cdot 10^{28}$$

In addition to steps 1 and 2 in the reaction (103), account should be taken also of the dissociation of the complex ion NH_4^+.

$$8NH_4^+ \rightleftarrows 8NH_3 + 8H^+; \quad pK_3 = 8pK_{NH_4^+} = 8 \cdot 9.2 = 73.6$$

and the formation of water

$$4H^+ + 4OH^- \rightleftarrows 4H_2O; \quad pK_4 = -4pK_w = -56$$

$$pK_{103} = pK_{102} + pK_3 + pK_4 = -28.06 + 73.06 - 56 = -10.46$$

$$K_{103} = 2.9 \cdot 10^{10}$$

To shift the equilibrium of reaction (103) to the right, hydrogen ions evolving in the reaction should be bound by additions of NH_4OH.

Filtered solutions that may be contaminated by ammonium complexes of zinc $Zn(NH_3)_4^{2+}$, nickel $Ni(NH_3)_6^{2+}$ and cobalt $Co(NH_3)_4^{2+}$, but are free from iron, are processed in autoclaves under pressure to settle out pure copper.

Autoclave Processing of Salvage Materials

Iron-bearing scrap and waste of complicated chemical composition can be processed to pure copper powder similarly to cement copper by leaching in autoclaves by the use of solutions of $(NH_4)_2SO_4$ and NH_3 with subsequent reduction by hydrogen.

Concentration of Lean Solutions Through Extraction

Lean (about 1 gram/litre Cu) highly contaminated copper solutions from underground, heap leaching or percolation are treated at some plants by extraction with the aid of a 7-10% liquor of benzophenoxin diluted with kerosene (a propriety product known as *Lix-64*). The organic phase is re-extracted by diluted sulphuric acid and processed by electrolysis. The electrolyte with up to 40 gram/litre Cu^{2+} is negligibly contaminated with iron and molybdenum and is practically free from zinc, arsenic and nickel. The

technique has not found extensive application as yet because of a high cost of the extraction agent and latter's relatively high losses with waste products.

Complex Ore Processing

Copper sulphide minerals tend to leach slowly and incompletely, while oxidized ore minerals cre sometimes poorly amenable to flotation. A combined flotation-hydrometallurgical technique that ensures the recovery not only of copper, but of noble metals as well, was suggested in 1931 independently by Prof. V. Mostovich and by a group of foreign researchers in specific application to the above ores. In short, the technique consists of leaching of oxidized minerals in agitators by sulphuric acid, cementation of copper by sponge iron directly from pulp and flotation of cement copper together with sulphide minerals and noble metals they contain.

Recovery of copper to a 20 to 65% concentrate, suitable for matte smelting in reverberatory or arc furnaces, ranges from 70 to 90% as against 30 to 40% in usual flotation. Some 2 to 3% of world copper output are obtained by the above technique.

Copper Electrolysis with Insoluble Anodes

Suitable for this technique are copper sulphate liquors obtained by various techniques, the only limitation being a content of not less than 30 gram/litre of Cu^{2+}, generally by leaching rich ores and concentrators in agitators.

Leaching is carried out in concrete tanks, lined with asphalt, ceramic tiles or sheet lead, and measuring up to 10 m in length, 1.2 to 1.4 m in width and depth. A tank holds about 80 starting sheets from pure copper and by an odd anode more, anodes being of a lead alloy with 8-15% Sb and 1% Ag. Liquor is supplied to each tank at the rate of about 1 m^3/min. Current density may be as high as 230 A/m^2, tank voltage, 2 to 2.4 V; current efficiency, 70 to 90%; consumption of electric power, 2000-3500 kWh/ton of copper.

The chemistry of the electrolysis has been already discussed (Para. 2). Current efficiency is greatly affected by

contaminating iron which is reduced at the cathode and oxidized at the anode (see reaction 22). If in small amounts, iron is settled out with the aid of lime and air oxidation according to reactions (100, 101) before the solution is processed by electrolysis. Large amounts of precipitate are difficult to wash, and this leads to excessive copper losses. When the concentration of trivalent iron is not too high, it is reduced as cement copper heated in agitators

$$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+} \qquad (104)$$

or in packed towers or scrubbers by sulphurous gas (roaster gases)

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+ \qquad (105)$$

In the electrolysis, divalent iron is oxidized at the anode at a lower potential instead of water, this being an advantage. However, the simultaneously originating ions Fe^{3+} reach the cathode and lower the current efficiency as to copper, thus raising power consumption.

As copper concentration in the electrolyte drops off, hydrogen evolves at the cathode together with copper because of concentration polarization. The deposit becomes spongy and darker from surface oxidation by dissolved oxygen and tends to peel off the cathode and settle as mud. Concentration polarization affects adversely the purity of the deposit as well. To avoid all this, electrolysis is discontinued after copper concentration falls to 15 or 20 gram/litre, and spent electrolyte with accumulated sulphuric acid is circulated in a leaching system and partly processed by cementation.

Leaching of Copper by Ammonia and Ammonium Carbonate Liquors

With lean oxidized and native ores, whose rock contains much calcium and magnesium carbonates, leaching with sulphuric acid is out of question since the consumption of acid would be too high.

It is then good practice to leach native copper by ammonia and ammonium carbonate liquors according to reactions (102, 103), and copper oxides and carbonates by a similar technique, but without the participation of oxygen. Reco-

very of copper may be as high as 80% and consumption of ammonia is about 80 kg per ton of ore with 4% Cu. Ammonia carbonate is here more advantageous than a sulphate since the complex it forms can readily be decomposed by steam

$$2Cu(NH_3)_4CO_3 + H_2O \rightarrow CuCO_3 \cdot Cu(OH)_2 + 8NH_3 + CO_2 \quad (106)$$

Copper hydroxide deposit is smelted with coal to metal, gases are cleaned and collected dust is recycled.

Flowsheets

Copper hydrometallurgy flowsheets practically used are most various and may consist of different processing stages depending on ore composition and local conditions. Fig. 41 illustrates a general hydrometallurgical flowsheet, its component steps, i.e., cementation or electrolysis, being used partly or wholly at many metallurgical plants. Before electrolysis, liquors are either completely cleaned of iron or reduced only by cement copper or SO_2. The flowsheet may also include an extraction or an autoclave processing of cement copper.

Hydrometallurgy Development Prospects

Chief shortcomings of wet copper recovery techniques are generally its failure to extract noble metals, small specific capacity and bulky equipment. In countries of hot climates the latter factor is of a lesser importance as leaching installations can be located in the open air.

As things stand today, 12% only of world copper output are produced from aqueous solutions. Along with this, some of hydrometallurgical processing stages are less costly than respective pyrometallurgical techniques because of absence or lesser consumption of fuel and refractories. Waste liquors are easier to neutralize than gases, and, therefore, there are less problems in meeting the present-day stringent antipollution requirements. Conversion to autoclave leaching and reduction will reduce the size of equip-

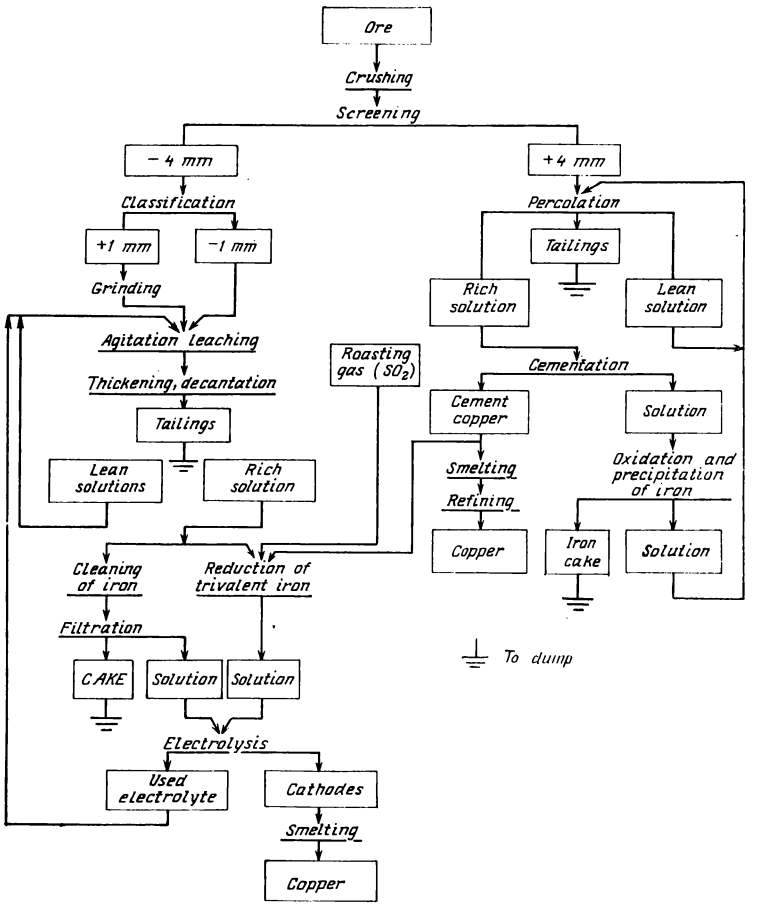

Fig. 41. General flowsheet of hydrometallurgy of copper

ment. A greater part will undoubtedly be played in the future by ion exchange and extraction techniques.

As yet, there is no clear-cut solution to side recovery of gold and silver, but some advances in this respect are already taking shape.

In all likelihood, hydrometallurgy will play an ever growing part in extractive metallurgy in the years to come.

Review Questions

1. What metals are generally associated with copper in ores?
Molybdenum, titanium, tungsten, zinc, lead, magnesium, gold, silver, tin, platinum.
2. What values are contained in copper ores?
Sulphur, bromine, selenium, phosphorus, tellurium.
3. What kinds of raw materials are of greatest importance in the metallurgy of copper?
Salvages and scrap, sulphide ores, oxidized ores.
4. What chief substances are mattes and slags composed of?
SiO_2, FeS, Al_2O_3, CaO, Cu_2S, MgO, ZnS.
5. Name modern methods for smelting copper mattes.
Blast furnace smelting, reverberatory furnace smelting of raw or roasted charge, flash smelting, electric furnace smelting.
6. Name impurities that are eliminated in fire and electrolytic refining of copper.
Fe, Au, Ag, Ni, S, Se, Te, Bi, Sb, Zn.
7. What reagents are used to leach copper out of sulphide and oxidized ores?
$(NH_4)_2SO_4$, H_2SO_4, $FeCl_3$, SO_2, $Fe_2(SO_4)_3$, NH_3.
8. Name leaching techniques suitable for rich and lean copper ores.
Percolation, autoclave leaching, leaching in agitators, heap and underground leaching.
9. Name impurities in solutions that interfere with the settling of copper by cementation and electrolysis.
H_2SO_4, Fe^{2+}, Fe^{3+}, Ni^{2+}.

CHAPTER 3

METALLURGY OF NICKEL

20. Chemical Properties of Nickel

Nickel is an element of group VIII, but it also is in the same period of the periodic table of elements as copper, being a transitional element of number 28. It follows then that chemical properties of copper and nickel are similar in many respects, but nickel is more active than copper.

Nickel was obtained for the first time by the Swedish chemist A. F. Cronstedt in 1751 who suggested the name for the element.

Natural nickel consists of five natural isotopes having atomic masses of 58, 60, 61, 63 and 64. Its average atomic mass is 58.71.

There are two known modifications of nickel. A common state of the metal, when it is forgeable and ductile, corresponds to the β-modification with face-centered cubic lattice. The other, α-modification, can be obtained from chemical compounds and alloys in the form of blackish grey powder. It has a hexagonal lattice and is stable at temperatures below 250°C.

According to its location in the periodic table, maximum valency of nickel is eight (group VIII), but in common compounds it is usually divalent. Tri- and tetra-valent nickel compounds are not stable, and nickel features higher valencies in complex ions only.

Electrochemical potential of nickel tends to point to its greater metallicity as compared to copper (Table 3).

Nickel is not oxidized in the air. It reacts slowly with hydrochloric and sulphuric acids to release hydrogen, but goes vigorously into solution in nitric acid. At the same time, concentrated nitric acid passivates the surface of nickel and enhances its resistance to attack by other acids. Nickel is not corroded by alkalis.

Nickel sulphide NiS, when heated to 600-700°C, dissociates with the formation of a solid solution of permanent composition

$$6NiS = 2Ni_3S_2 + S_2$$

These and other less stable nickel sulphides Ni_3S_4, Ni_6S_5 are used as catalysts in the manufacture of organic products. At metallurgical processing temperatures the only stable nickel sulphide is Ni_3S_2 which in oxidizing roasting turns to NiO, frequently by way of an intermediate compound $NiSO_4$.

Nickel sulphate $NiSO_4$ or $NiSO_4 \cdot 7H_2O$ (nickel vitriol) is well soluble in water, its solutions being used for nickel plating steel and other metals to protect them against corrosion or improve their appearance.

Nickel protoxide NiO is insoluble in water, but dissolves in strong acids. Calcination at temperatures in excess of 1000°C greatly lowers the chemical activity of NiO. Nickel protoxide can readily be reduced to metal by carbon and hydrogen at temperatures of 600-700°C.

Hydrolysis of aqueous solutions of nickel salts gives a precipitate $Ni(OH)_2$, which is readily soluble in acids and in aqueous ammonia with the formation of blue-coloured complex ions $Ni(NH_3)_4^{2+}$, $Ni(NH_3)_6^{2+}$, etc. Similar complex ions are obtained by the action of aqueous ammonia on freshly reduced metallic nickel powder in the presence of oxidizing agents.

If nickel salts are hydrolyzed and simultaneously acted upon by an oxidizer, e.g., chlorine, the result is a deposit of black hydroxide $Ni(OH)_3$ which is used in the manufacture of alkali storage batteries.

According to the above industrial classification, cobalt is referred to "junior" metals. However, some 80% of its output in the Soviet Union are obtained as by product of nickel ores, and, therefore, metallurgy of cobalt is dealt with in the present chapter.

The yearly world output of cobalt is by about 15 times less than that of nickel, and it costs three times as much as the latter. Although very close in chemical properties to nickel, cobalt has its valuable particularities and special applications.

The intermediate position of cobalt in the metallic triad of iron—cobalt—nickel and its oxidation-reduction potentials (Table 3) tend to indicate its similarity with iron and nickel, particularly with the latter.

Cobalt forms oxides CoO, and Co_3O_4 and sulphides CoS, Co_2S_3, Co_3S_4 and CoS_2. Its affinity for oxygen and sulphur is a midpoint between iron and nickel. Its affinity for oxygen is higher than that for sulphur.

When an oxidizing agent acts upon sulfide or metallic melts, containing iron, cobalt and nickel in equal concentrations, the first to oxidize is iron, as shown by the reaction

$$Fe + CoO \rightleftarrows FeO + Co \qquad (107)$$

Difference in the affinities explains the transfer of cobalt to converter slags after slagging of the bulk of iron and the reduction in the first place of cobalt when molten slag, containing equal concentrations of Fe and CoO, is processed with reducing agents.

The oxidizing ability of $Co(OH)_3$ is greater than that of $Fe(OH)_3$, but lower than that of $Ni(OH)_3$, and, therefore, the reactions below are possible in solutions

$$Ni(OH)_3 + Co^{2+} \rightarrow Ni^{2+} + Co(OH_3) \qquad (108)$$

$$Co(OH)_3 + Fe^{2+} \rightarrow Co^{2+} + Fe(OH)_3 \qquad (109)$$

Cobalt greatly enhances heat-resistance and high-temperature strength of steels, inclusive of chromium-nickel steels. Properties of high-speed steels alloyed with tungsten, chromium and molybdenum, are greatly improved by addition of cobalt. Cobalt alloys are used to manufacture permanent magnets of high magnetic power, such as Alnico-24 (50% Fe, 24% Co, 14% Ni, 9%Al and 3% Cu). An alloy with 75% Co, 13% Si, 7% Cr and 3% Mn is more resistant to corrosion in strong acids than platinum. There are also many other valuable properties of cobalt.

Cobalt is also used in the form of salts and oxides, as a component of catalysts for organic syntheses, of drying agents for varnishes and oil paints and for the manufacture of weather-resistant enamels and paints. Radioactive isotope Co^{60} is used in medicine to treat malignant tumors. Most of cobalt salts are required for a normal development of plants and animals.

21. Nickel Ores and Their Dressing

Ore nickel minerals, sulphides and silicates, form sulphide and oxidized nickel ores.

Nickel in *sulphide ores* is represented by a mineral pentlandite (an isomorphic mixture of iron and nickel sulphides—(Ni, Fe)S), and to a lesser extent also by solid solutions of nickel in pyrrhotite Fe_7S_8. Other sulphide minerals are of a minor importance. Nickel is accompanied in these ores by copper (chiefly as chalcopyrite), cobalt and metals of the platinum group, among them platinum, osmium, iridium, rhodium, ruthenium and palladium.

Nickel content in sulphide ores varies from 0.8 to 5.5%; copper, 0.6% to 10%; cobalt, up to 0.2% (Table 14).

Table 14

Chemical Composition of Copper-Nickel Ores, %

Ore	Ni	Cu	Co	S	Fe	SiO_2	Al_2O_3	MgO	CaO
1	5.6	1.8	0.16	28	45	10	7	1.5	1
2	2.25	1.0	0.04	20	30	22	6	19	2
3	0.8	0.5	Traces	2	11	41	—	1.2	—

In sulphide copper-nickel ores, nickel is accompanied by pyrrhotite, magnetite and silicates of iron, aluminium, magnesium. Similarly to copper ores, they are subdivided into massive, pyritic and disseminated (minute metal sulphide particles disseminated in a basic or ultra-basic rock) ores.

Copper-nickel ores are beneficiated by magnetic separation, by bulk and differential flotation, products being either a copper-nickel concentrate or two concentrates, a copper and a nickel one. Because of an intimate mutual intergrowth, minerals are often impossible to separate by flotation. Copper concentrates are almost uncontaminated by nickel, but nickel concentrates frequently carry relatively large amounts of copper.

Nickel is to be separated from copper in metallurgical processes in one way or another, and so ores are sometimes

treated to a collective concentrate, this obviating the need for a complicated selective flotation.

Nickel-bearing pyrrhotite is magnetic, and it is sometimes separated before flotation by electromagnetic means. In a magnetic concentrate, nickel content may be as high as 2.5%, copper, 1.5%, size of concentrate lumps being 25 to 60 mm.

Tailing of magnetic separation or ore (if no magnetic constituents can be advantageously separated) is ground and flotated.

Selective flotation with the manufacture of two concentrates is used if copper content is relatively high.

At some concentrators, flotated first is the chalcopyrite, nickel minerals being left in the pulp. At others, a bulk concentrate is obtained first, then separated by re-flotation. When chalcopyrite is floated as froth, floating properties of the pyrrhotite and the pentlandite are suppressed by adjusting alkali content of pulp through additions of soda.

Bulk flotation may also be effected in an alkali pulp. Pyrrhotite may be activated by sodium sulphide and copper sulphate. Collector is a xanthate, and frother, pine oil. Tentative compositions of copper-nickel and nickel concentrates are given in Table 15.

Flotation recovery of copper and nickel may attain 90%, and up to 80% Co may also be extracted to concentrates.

Table 15

Chemical Composition of Concentrates, %

Concentrate	Ni	Cu	Co	Fe	S	SiO_2	Al_2O_3	CaO	MgO
Copper-nickel	5.5	3.5	0.17	30	20	20.0	1.5	0.5	12
	10	5	0.1	37	27	15	1.0	0.5	3
	3.2	1.8	0.13	—	—	—	—	—	—
Nickel	12	2	0.3	30	35	28	—	—	—
Copper	1.6	30	—	30	33	2	—	—	—

Oxidized or weathered crust ores contain nickel as an isomorphic mixture of hydrated silicates of nickel and magnesium of the type $n\mathrm{NiSiO_3}\cdot m\mathrm{MgSiO_3}\cdot\mathrm{H_2O}$, which

forms garnierite, nepouite, revdinskite and other similar minerals. Copper may also be sometimes represented in these ores, but in very small amounts. Cobalt accompanies nickel in these ores as well, its oxides being often associated with manganese minerals. Nickel content in oxidized ores is generally 0.9 to 1.5% by dry mass, and that of cobalt, up to 0.15%.

Gangue of oxidized ores consists of hydrated iron oxides, alumosilicates, quartz and talc. Ores feature an earthy structure, low strength of lumps and high hygroscopicity.

Competitive nickel oxidized ores are yet to be developed, and, therefore, they are directly treated by metallurgical techniques. Chemical composition of typical nickel oxidized ores is given in Table 16.

Table 16

Chemical Composition of Typical Oxidized Nickel Ores, %

Ore	Ni	SiO_2	MgO	Fe_2O_3	CaO	Al_2O_3	S
1	1.1	28	0.5	15	3	19	0.1
2	1.0	38	1	18	2	21	0.1
3	1.6	45	16	19	0.5	0.5	—

22. Nickel Manufacturing Techniques

Sulphide ores and concentrates and oxidized ores may be processed by a variety of techniques, both pyrometallurgical and hydrometallurgical.

Matte Smelting of Sulphide Ores and Concentrates

Ores with a total content of more than 2 to 5% of copper and nickel are considered rich, and they are smelted directly, with no treatment whatsoever.

Ores and concentrates contain same minerals, and they may be treated by the similar techniques.

As ore is heated to 400-600°C, even before it starts melting, chalcopyrite (58) and nickel-bearing sulphides decom-

pose

$$6(NiS,\ FeS) \rightarrow 2Ni_3S_2 + 6FeS + S_2 \qquad (110)$$

$$2Fe_7S_8 \rightarrow 14FeS + S_2 \qquad (111)$$

The result of these reactions is that a complicated aggregate of minerals is converted to a mixture of plain sulphides: Ni_3S_2, Cu_2S and FeS.

At temperatures necessary to melt a slag composed of gangue oxides and fluxes, copper, nickel and iron sulphides are completely soluble in each other. They form a copper-nickel matte that may be separated from slag as a heavier liquid layer.

If sulphur is partly oxidized in smelting or in a preliminary roasting, the distribution of copper, nickel and iron between the matte and the slag will be governed by the affinities of these metals for oxygen and sulphur. Under smelting conditions, the affinity for sulphur, which determines the possibility of a metal passing to matte, of copper is higher than that of nickel, while that of nickel is higher than the affinity for sulphur of iron. By contrast, the affinity for oxygen of the same metals decreases in a reverse order. If the amount of sulphur is insufficient to sulphidize all the metals, the first to pass to matte will be copper, then nickel, and, finally, iron. The greater the quantity of iron passing to matte, the greater the effectiveness of sulphidizing of copper and nickel, but matte with much iron sulphide will necessarily be low in copper and nickel. To transfer nickel to matte as completely as possible in smelting of ores and concentrates, iron is slagged but partly in order to leave some of it for the matte.

As to affinity for sulphur and oxygen, cobalt is in an intermediate position between iron and nickel.

Molten matte is blown through in a converter with additions of quartz. Iron oxidizes and is slagged by silica.

The chief product of converting is a copper-nickel matte, i.e., an alloy of copper and nickel sulphides with 1 to 3% of iron.

Cobalt is partly slagged together with iron in converting.

Converter slags are sometimes processed separately to recover cobalt. Noble metals concentrate almost entirely in the copper-nickel matte.

Once cooled, the copper-nickel matte is crushed, ground and flotated to yield two concentrates, a nickel one composed of almost pure Ni_3S_2 and a copper one containing

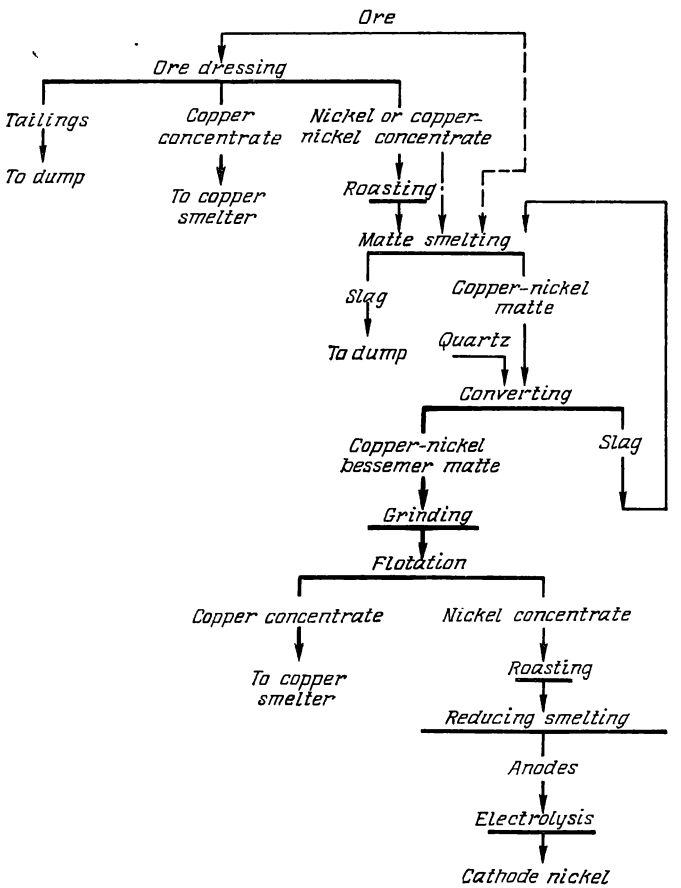

Fig. 42. Flowsheet for treatment of sulphide copper-nickel ores

Cu_2S. The latter is processed to copper, similarly to common copper concentrates by smelting to matte and blowing through in converters.

Nickel concentrate is oxidized through roasting according to the reaction

$$2Ni_3S_2 + 7O_2 = 6NiO + 4SO_2 \qquad (112)$$

The resultant nickel oxide, a grayish powder, which also carries cobalt oxides and noble metals is reduced to metal by coal in electric furnaces, then cast to anodes.

Nickel anodes are refined by electrolysis, cobalt and remaining copper being extracted from the electrolyte, and platinum group metals from anode mud.

Smelting of copper-nickel matte from sulphide nickel ores and concentrates is illustrated by the flowsheet in Fig. 42.

Rich large-lump copper-nickel ores are smelted to matte in blast furnaces, provided ore gangue is not too refractory. In some instances, ores that run much magnesium oxide or other refractory constituents can be smelted in electric furnaces only.

Flotation concentrates and small-size fractions of rich ores are smelted in reverberatory or electric furnaces, the materials being given a preliminary roasting if their sulphur content is high.

The choice of the smelting technique greatly depends on the composition of raw materials and local economic conditions, in particular, on availability of fuels and electric power cost.

Hydrometallurgical Processing of Sulphide Ores

In this technique, ground ore or concentrate is treated by a solution of ammonia and ammonium sulphate $(NH_4)_2SO_4$ in autoclaves at a gauge pressure of about 506.7 kN/m^2 (7 atm). Copper, nickel and cobalt pass into solution as complex ammonium salts, e.g., according to the reaction

$$NiS + 2O_2 + 6NH_3 \rightarrow Ni(NH_3)_6SO_4 \qquad (113)$$

Vigorous oxidation of sulphides releases heat which is extracted by coolers to maintain a temperature of 70-80°C in the autoclave. The sulphur of the concentrates oxidizes in the process to $S_2O_3^{2-}$, $S_3O_6^{2-}$ and SO_4^{2-}, while iron precipitates as a hydroxide and basic sulphates.

Filtered solution is boiled to settle out copper according to the reaction

$$Cu^{2+} + 2S_2O_3^{2-} = CuS + SO_4^{2-} + S + SO_2 \qquad (114)$$

Next, copper remaining in the solution is settled out by hydrogen sulphide, and the purified solution, carrying nickel and cobalt, is treated in autoclaves by hydrogen at a pressure of about 2.5 MN/m^2 (25 atm) and temperature of approximately 200°C.

First to settle as particles 2 to 80 micrometres across is the bulk of nickel

$$Ni(NH_3)_6^{2+} + H_2 \rightarrow Ni + 2NH_4^+ + 4NH_3 \qquad (115)$$

Once the precipitate is filtered, the remaining nickel and cobalt are extracted through a hydrogen sulphide treatment.

A further processing of the sulphide precipitate in the autoclave by oxygen and ammonium dissolves cobalt. The insoluble deposit, composed chiefly of nickel sulphide, is returned to basic leaching, while cobalt is extracted from the solution by the combined action of hydrogen and pressure.

The flowsheet is complicated and requires costly equipment, but it allows a recovery of about 95% Ni, about 90% Cu and 50 to 75% Co.

Matte Smelting of Oxidized Ores

Now the most widely used technique for processing nickel oxidized ores by matte smelting is based on the difference in affinities of iron and nickel for oxygen and sulphur.

Nickel is sulphidized and transferred to matte, an alloy of Ni_3S_2 and FeS,

$$6FeS + 6NiO \rightarrow 6FeO + 2Ni_3S_2 + S_2 \qquad (116)$$

while the bulk of the iron is removed with the slag according to reaction (82).

Oxidized ores carry no sulphur, and, therefore, it is introduced in smelting through additions of pyrite or gypsum. The latter is reduced to calcium sulphide and sulphidizes iron and nickel in the process. In smelting, the action of gypsum is more complicated than that of pyrite, but

gypsum is generally preferred as it is cheaper and gives no highly ferrous heavy slags.

But the sulphidizing agent which provides a greatest advantage in the nickel oxidized ores smelting is the local cobalt-bearing pyrite that is low in copper and carries no noble metals.

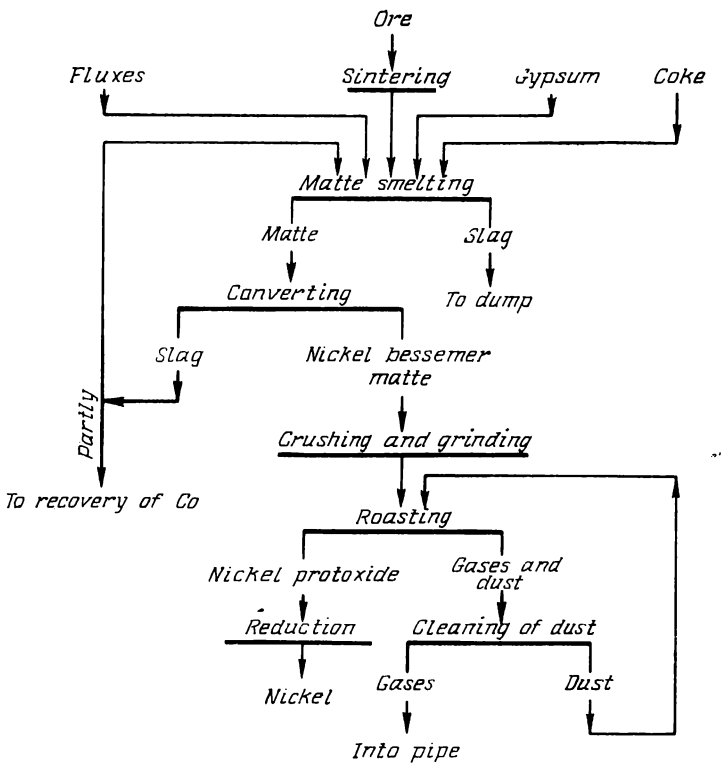

Fig. 43. Flowsheet for treatment of oxidized nickel ores

Nickel matte resulting from smelting ores with pyrite or gypsum contains up to 60% Fe which is then separated from nickel by blowing through of molten matte in a converter. In converting, iron is selectively oxidized and slagged by quartz additions, the product being practically pure

copper-nickel matte, free from iron. The converter slag is high in nickel, and it is returned to ore smelting or processed separately to recover cobalt.

Copper-nickel matte is cast into moulds, then crushed and given a dead roast:

$$2Ni_3S_2 + 7O_2 \rightarrow 6NiO + 4SO_2 \qquad (117)$$

Nickel protoxide is mixed with a reducing agent low in sulphur, e.g., with pertroleum coke, and smelted in an electric furnace at 1500°C to yield molten nickel. The flow-sheet for processing oxidized nickel ores is presented in Fig. 43.

Nickel is cast into anodes for refining by electrolysis or granulated by pouring it in a thin jet into water.

Smelting of Oxidized Ores to Nickel Cast Irons (Ferronickel)

Rich oxidized ores are sometimes smelted in electric furnaces with additions of coal to reduce all of the iron, nickel and cobalt to a naturally alloyed cast iron.

Relatively lean ores are similarly smelted in pig-iron blast furnaces, but the technique finds a limited use.

Despite a wide use of nickel in special steels, its smelting as an alloy with iron is not always acceptable, since cobalt, manganese, chrome and other elements pass into the alloy, their uncontrolled combinations allowing but rarely adequate utilization of their valuable properties.

Processing of Oxidized Nickel Ores by Puddling

In this technique, a mixture of ore, coal and coke fines is heated in rotary kilns (similar to that shown in Fig. 94) to a temperature of 1250-1350°C, this allows reducing nickel, cobalt and a part only of iron. The reduced metals are obtained as grains (balls) mixed with half-molten slag. Once cooled, the mass is crushed and the ball alloy is extracted by electromagnets. The technique has found no extensive application for the same reasons as the above one, since no separate recovery of cobalt is possible.

Hydrometallurgy of Oxidized Ores

In one of the methods, known in technical literature as the Cuban technique, ground ore is treated by a reducing roasting in mechanical multi-hearth roasters in an atmosphere of generator gas. At 720-750°C, nickel and cobalt are reduced to metals, but iron, to ferrous oxide only. The calcine is leached by a solution of ammonia in the presence of carbon dioxide and air oxygen. Nickel forms water-soluble ammoniates

$$2Ni + 12NH_3 + 2CO_2 + O_2 \rightarrow 2Ni(NH_3)_6CO_3 \quad (118)$$

After gangue is separated by dewatering and washing, the liquor is treated by live steam. Excess ammonia is removed in the process, and basic nickel carbonates precipitating as a result of hydrolysis

$$2Ni(NH_3)_6CO_3 + H_2O \rightarrow NiCO_3Ni(OH)_2 + CO_2 + 12NH_3 \quad (119)$$

The deposit is calcinated in rotary kilns to yield nickel protoxide which contains some cobalt. Ammonia in the gases is absorbed by water and recycled to leaching. Nickel protoxide is agglomerated in sintering machines and as sinter supplied to steelmaking plants. Nickel recovery may attain 75%, and that of cobalt, 20%.

Such a poor performance, especially as regards cobalt, has limited the application of the technique.

Another hydrometallurgical flowsheet, introduced industrially in 1959, has also been developed in Cuba. Natural fine ore with 1.3% Ni and 0.14% Co, containing little MgO, is sized, then leached in autoclaves by a 30% sulphuric acid. At a temperature of 240°C and a steam pressure of 37 gauge atm., up to 95% each of nickel and cobalt and less than 1% of iron pass into the liquor. The low extraction of iron is due to the hydrolysis of Fe^{3+} with the formation of barely soluble basic sulphates or hydroxide according to the reaction (101)

$$[Fe^{3+}] \approx a_{Fe^{3+}} = \frac{a^3_{H^+} \cdot SP_{Fe(OH)_m \cdot (SO_4)_n}}{K^3_w}$$

The ionic product of water rapidly rises with the temperature, i.e., at 25°C, $pK_w = 14$, and at 100°C, 12.26. A fact not to be omitted is that the product $Sp_{Fe(OH)_m \cdot (SO_4)_n}$, still unknown, is likely to increase with the temperature either. However, experience tends to indicate that hydrolysis of trivalent iron proceeds to a high degree even for pH $\approx$ 1.

Pulp from the autoclaves is thickened and decanted. The liquor is reduced by hydrogen sulphide

$$2Fe^{3+} + H_2S \rightarrow 2Fe^{2+} + 2H^+ + S^0 \qquad (120)$$

then neutralized by limestone. After clarification in thickeners, nickel and cobalt are settled out by hydrogen sulphide in autoclaves at a pressure of 10 atm and temperature of about 125°C. The latter process corresponds generally to the reaction

$$Me^{2+} + H_2S \rightleftarrows MeS + 2H^+ \qquad (121)$$

$$K = \frac{a^2_{H+}}{a_{Me^{2+}} \cdot [H_2S]} = \frac{K_{HS^-} \cdot K_{H_2S}}{Sp_{MeS}}$$

$$[Me^{2+}] \approx a_{Me^{2+}} = Sp_{MeS} \frac{a^2_{H+}}{K_{HS^-} \cdot K_{H_2S} \cdot [H_2S]}$$

It is then readily apparent that the residual concentration of metal depends, all other conditions being the same, on the value of Sp_{MeS}

As no high-temperature data are available, given below are values relative to 20-25°C

MeS	NiS	CoS	FeS	CuS	ZnS	MnS
pSp	25.7	24.7	17.3	35.2	23.8	12.6

This explains the possibility of simultaneous deposition of copper and zinc sulphides and a lesser probability of the presence of iron and manganese. The deposit is a finished product, a nickel-cobalt concentrate.

23. Smelting of Nickel from Sulphide Ores and Concentrates

Concentrates and fine ores containing relatively easy-melting gangue and requiring no excessive fluxing are smelted in reverberatory furnaces.

Electric smelting is used for charges that tend to produce rather refractory slags, as ores and concentrates high in magnesium oxide. Smelting of such ores and concentrates in reverberatory furnaces calls for large amounts of fluxes with resultant increase in losses of nickel and copper with slags. By contrast, a higher temperature can be maintained in electric furnaces, making feasible operation on refractory slags. However, electric smelting is competitive, if cheap electric power is available locally.

Roasting of the charge before it is smelted in reverberatory or electric furnaces is imperative, when a direct processing fails to yield a rich matte because of a high content of iron sulphide.

Reverberatory smelting of copper-nickel materials differs little from copper smelting. Sulphur is oxidized chiefly at the expense of oxygen contained in the higher iron oxides. In smelting of raw concentrates and ores, sulphur is also removed through dissociation of higher sulphides.

Basically, smelting involves reactions among copper (79) and nickel oxides, on the one hand, and iron sulphide, on the other hand, as a result of which copper and nickel pass to matte, and iron, to slag

$$6NiO + 6FeS + 2O_2 + 3SiO_2 \rightarrow 2Ni_3S_2 + 3Fe_2SiO_4 + 2SO_2 \quad (122)$$

Distribution of the metals between matte and slag is governed by their affinities for oxygen and sulphur.

The difference in affinity for oxygen and sulphur, given by the value $\Delta Z^{\circ}_{MeO} - \Delta Z^{\circ}_{MeS}$ per mole of metal for equal activities of sulphide and of oxide, may serve as a criterion of predominant sulphidizing or oxidation of a metal. Data below tend to indicate that the order of passage to slag corresponds to the series Fe > Ni > Cu, and to matte, to Cu > Ni > Fe:

Metal	Fe	Ni	Cu	kj/g-atom *Me*
$\Delta Z^0_{MeO} - \Delta Z^0_{MeS}$	−121	−84	+25	

An adequate recovery of nickel and copper to matte can be attained against a desulphuration that results in a partial only slagging of iron. Besides, the richer a matte, the greater the losses in slags. Therefore, in matte smelting no complete slagging of iron is aimed at.

Cobalt behaves in smelting similarly to nickel and concentrates in the matte.

Copper-nickel and copper smelting reverberatory furnaces are similar in design, as are their capacities. Smelting power for roasted copper-nickel charges attains 4.5 t/m^2 of hearth area, against a fuel consumption (in terms of reference fuel) of 11-12%.

Electric smelting is carried out in rectangular furnaces. Three or six self-baking* continuous electrodes, up to 1200 mm in diameter and arranged in a single line, pass through the furnace roof and dip into molten slag (Fig. 44) which serves as a resistor.

The bath temperature is controlled automatically at a preset current intensity with the aid of a device which adjusts immersion of electrodes. Additionally, the temperature can be controlled by varying the power supply voltage up to 800 V and adjusting the charging and the slagging schedules.

The charge is introduced through roof openings onto the banks or near the electrodes or directly upon the electrodes if an easy-melting gangue is involved. Depth of slag layer is maintained within 1.4 to 2.5 m to allow ready temperature control.

Smelting power of electric furnaces for every 1000 kVA of installed capacity may attain 30 tons of charge per sq. metre of hearth area, and the consumption of power, 600 to 800 kWh/t of charge. Recovery to matte of copper, nickel and noble metals may be as high as 97% owing to a relatively small fall of slag and low dust losses.

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* Self-baking carbon electrodes are described in Para. 49.

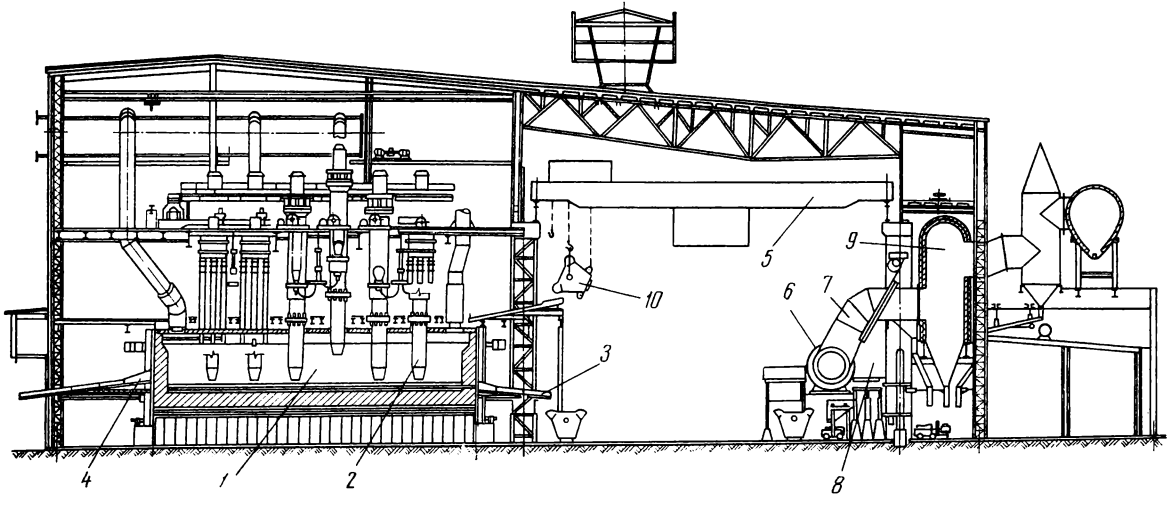


Fig. 44. Section through electric smelting plant

1—electric furnace; *2*—electrodes; *3*—matte taphole; *4*—slag taphole; *5*—overhead crane; *6*—converter; *7*—converter hood; *8*—tuyere punching platform; *9*—settling chamber and flue; *10*—ladle for pouring converter slag

Modern electric furnaces for copper-nickel smelting are available in ratings from 15 to 48 MV, hearth area for the latter rating being 25 × 6.5 m².

Smelting in blast furnaces is advantageous for large-lump rich ores when a cheap coke, a consumption of 9 to 11% of the mass of the charge, is available. Copper-nickel blast furnace smelting is similar to copper semipyritic smelting. Due to greater pyrrhotite content and elevated coke consumption, the desulphuration is lower than in copper smelting and the resultant mattes are lower in metal content.

A thorough size-sorting of ore and sintering of fines and concentrates ensure smelting of mattes of an aggregate copper and nickel content of 15 to 25%. Smelting of richer mattes would have been disadvantageous because of high metal losses in slags.

Aggregate content of copper and nickel in slags is below 0.2-0.4%, but owing to a high fall of slag per unit mass of matte, the recovery of copper, nickel and noble metals to matte may attain 90% for richer ores only.

Smelting power of furnaces varies over a wide range and depends, among other factors, on the composition and the care given to the preparation of the charge. Smelting power is higher for sinter as compared to raw charge. In practice, some 70 to 110 tons of charge are smelted in 24 hours for every sq. metre of furnace area at tuyere level. Tentative compositions of slags from smelting of sulphide ores in different furnaces are given in Table 17.

Blowing of copper-nickel matte in converters. Irrespective of the technique a copper-nickel matte is smelted by, it is an alloy of copper, nickel and iron sulphides that contain dissolved ferrites, cobalt sulphide and platinum group metals. The matte also carries some dissolved gangue oxides. Sulphur content in copper-nickel mattes is close to 25%, and the V. Mostovich rule is applicable to them.

The aim of converting is to oxidize and slag iron only in order to obtain an iron-free copper-nickel bessemer matte. Converters used for this purpose do not differ from those known in the metallurgy of copper.

In accordance with the difference in affinity for oxygen and sulphur, iron is the first to pass to converter slag and is followed by cobalt. With the aim to leave the bulk of cobalt

Table 17

Composition of Slags from Various Smelting Techniques

Smelting technique	Composition of slag, %						
	Ni	Cu	SiO_2	FeO	CaO	Al_2O_3	MgO
Blast furnace smelting of sulphide ores	0.12	—	39	38	7	0.12	12
Reverberatory smelting of copper-nickel concentrates	0.20	0.07	36	52	3	0.08	6
Electric smelting of sulphide ores	0.07	0.05	45	25	2	0.06	3

in the copper-nickel matte not all of the iron is oxidized, the blow through being discontinued before all of iron passes to slag.

Converter slags are twice re-smelted in electric furnaces on a layer of lean matte which is recycled, while slag is dumped. The effect of this treatment is that about 60% cobalt of the ore is recovered to copper-nickel matte. Considering cobalt's low content in the ore, the recovery may be accepted as satisfactory.

Next, cobalt and platinum metals, which always accompany nickel, are separated in electrolytical refining.

Copper-nickel matte is an alloy of copper and nickel sulphides, and it generally contains 3-4% Fe and about 22% S.

24. Flotation of Copper-Nickel Mattes

As already mentioned, a copper-nickel matte is an alloy of sulphides Ni_3S_2 and Cu_2S carrying some iron, cobalt and platinum metals. A matte may have a following composition: 45% Ni; 28% Cu; 1% Co; 3% Fe; 21% S; 2% other elements.

In slow cooling of molten copper-nickel matte under a blanket of sand over a period of 36 to 40 hours the conditions are right for growth of Cu_2S crystals. In the solidified matte, which carries cuprous sulphide as large grains, the

latter is crushed to a mixture of Cu_2S, Ni_3S_2 and a Ni + Cu alloy particles that can readily be separated by flotation.

Flotation is carried out in a soda liquor at pH = 12. The collector is butyl xanthate whose surface films on the cuprous sulphide are stable, and on the nickel sulphide, unstable. A copper concentrate passes to froth, while Ni_3S_2 and alloy particles remain in the pulp. Bulk copper concentrate is given several cleanings, while the nickel concentrate is refloated in a number of stages. Examples of yields and compositions of flotation products are given in Table 18.

Table 18

Example of Copper-Nickel Matte Flotation

Product	Yield, %	Composition, %			Recovery, %		
		Cu	Ni	Co	Cu	Ni	Co
Converter copper-nickel matte	100	26	48	1.1	100	100	100
Nickel concentrate	68	3	68	1.5	8	96	92
Copper concentrate	32	74	4	0.2	91	3	7

Copper concentrate can be smelted in reverberatory or electric furnaces to a practically finished white matte. The concentrate can be charged as grains into a converter in blowing through of copper mattes.

Nickel concentrate is roasted in fluid-bed roasters, pelletizing preceding the roast to reduce dust formation*.

Nickel sulphide is oxidized by air oxygen according to reaction (112).

The fluid-bed is maintained at a temperature of about 1000°C. Up to 35% of the charge is entrained as dust, which is collected in cyclones and electric precipitators then returned as the roaster feed. The calcine runs some 0.1% of sulphur.

Nickel protoxide of the calcine can be reduced at low temperatures, but as it is necessary to obtain a liquid nickel, the reduction is carried out in electric three-phase arc furnaces at a temperature of about 1500°C. The reducing agent is low-sulphur coal, charcoal or petroleum coke.

* Pelletizing, or cold granulation, is described in Para. 31.

Three-phase circular electric furnaces with a water-jacketed roof are built in ratings from 2000 to 5000 kVA. Walls and hearth are lined with magnesite brick, and 350-mm dia graphite (carbon) electrodes are used. A charge is supplied by a feeder throughout smelting via a central opening in the roof between the electrodes. Treatment time for a yield of about 8.5 tons of nickel is 6 to 8 hours, electric power consumption being approximately 1100 kWh per ton of nickel.

Limestone is added to flux off the unavoidable small amounts of impurities and to remove completely the remaining sulphur. Silica, alumina and other oxides that pass to nickel oxide because of roaster lining wear are slagged to give a small quantity of basic lime slag which carries 0.2 to 0.4% Ni.

Slag is skimmed after the charge is smelted, and carbon that dissolves in the nickel is oxidized by an addition of NiO, the metal then being cast into anodes for electrolytical refining or granulated by pouring into a water tank fitted with wire baskets.

25. Smelting of Nickel from Oxidized Ores

The charge for blast furnaces should of necessity be in lumps, and, therefore, ores, which are commonly moist loose earthy masses, are agglomerated prior to smelting. Briquetting, one of the many agglomeration techniques, is pressing of ores to oval, cylindrical or variously shaped lumps, or briquettes, weighing up to 0.2-0.3 kg each. The binder is the clay of the ore. Ore is ground and dried before it is briquetted.

Ore is mixed with gypsum or pyrite prior to briquetting as uniformity of charge composition has a favourable effect upon subsequent smelting. Briquettes being shaped in roll (Fig. 45) or other presses. Briquetting is sometimes unsatisfactory as briquettes are mechanically weak. They tend to disintegrate inside the furnace to fines which hamper the latter's operation. Another shortcoming is a small gas permeability of briquettes.

Roll presses provide a pressure of up to 100 kg/cm^2, and the resultant briquettes withstand, once dried, loads of up

to 12 kg. More efficient punch presses raise the former parameter to 500 kg/cm², and the latter, to 40 kg. Briquettes may also be strengthened by air drying for 3 days or by a relati-

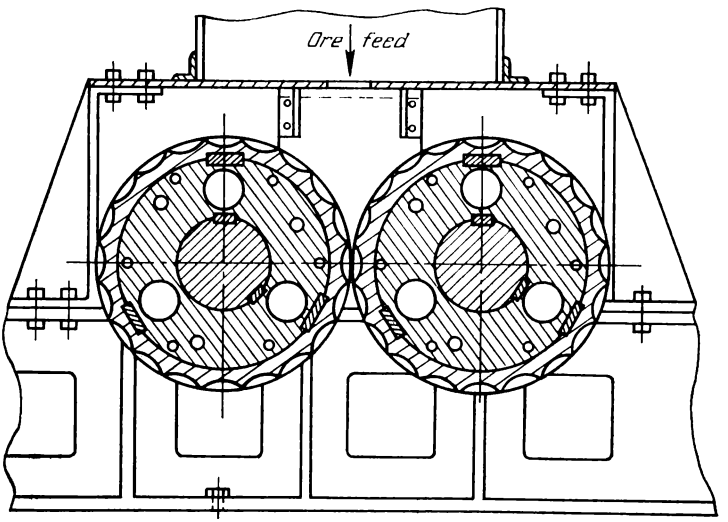


Fig. 45. Roll-type briquetting press

vely short-time heating. Some operators find it expedient to add coal fines to briquettes as it tends to bring down consumption of the costly coke in subsequent smelting.

Ore Sintering

Agglomeration by sintering was introduced for the first time ever into nickel manufacture in the USSR. Sintering machines are used also in the metallurgy of other nonferrous metals.

A grate-bottom car or pallet, the chief component part of sintering machines, can readily be observed in Fig. 46. The steel or cast iron trough of the car carries no end walls and resembles a short trough with a bottom of iron grates. The pallets are mounted on rails and their edges are pressed tight against the sides of a steel chamber that is connected to an exhauster, or a fan that sucks gases.

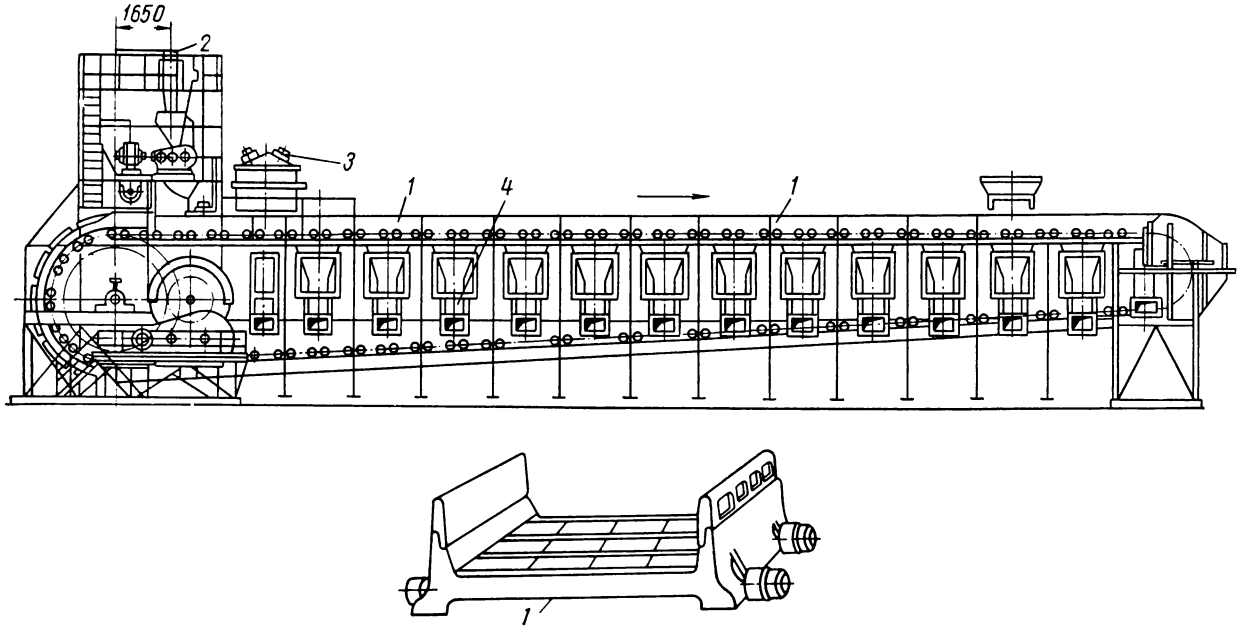


Fig. 46. Sintering machine

1—pallet car; *2*—feed hopper; *3*—ignition furnace; *4*—wind boxes

Ore mixed with a fine fuel (coal or coke) is charged onto the grates in a bed up to 30 cm thick. The exhauster builds up a vacuum inside the chamber and thus sucks air through the charge bed. The fuel is ignited from the top by directing an oil or gas flame upon it, combustion then proceeding into the body of the bed as air is sucked. Charge temperature rises to 1100-1400°C depending on fuel content, both oxidation and reduction being possible. The oxidizing agent is oxygen of the air that is sucked through, and the reducing agent, fuel carbon. When fuel content is relatively small, oxidation predominates, and when fairly high, reduction may take place.

In order to sinter a nickel ore, it is necessary to partially reduce constituent iron oxides Fe_2O_3 and Fe_3O_4 to FeO.

Ferrous oxide combines with silica to give easy-fusing silicates that melt at about 1100°C. Droplets of this melt originate in the body of the solid charge and wet the surrounding particles. As soon as fuel burns out and the temperature goes down, the silicate melt solidifies to cement together the solid particles and thus cake the charge into a strong porous sinter. When the car is tilted, the sinter is dumped as a porous lump.

Sintering machine cars are placed on the horizontal stretch of the rail framework close to one another to form a continuous trough of some length bordering on the sides of a common wind box (Fig. 46).

The cars move slowly at a speed of 1.4-4.5 m/min. At the beginning of its travel, the extreme left-hand pallet car passes first underneath feed hoppers where it is charged. Further on, the car passes over a wind box and simultaneously underneath an igniter. The charge ignites, and sintering begins. Fuel burns out before the car reaches the last wind boxes, sintering then coming to its end and the sinter being cooled by the air that is sucked through. At the end of its horizontal path the car's rollers slide beneath a curved stretch of rail tracks so that the car rolls down, turns over and bumps against the preceding car to dump the sinter out. The car next slides along a bottom sloping stretch of tracks where car's rollers engage into a passage between teeth of two sprocket wheels actuated by a motor. The

sprockets lift the car into initial position, i.e., underneath the feed hoppers.

The travel speed is adjusted by the rotation speed of the sprockets as a function of charge composition and required sintering rate. Above the wind box the cars travel at a speed of about 3 m/min.

Sintering machines are described by the length and the width of wind box whose surface area may be as large as 200 m^2, but is generally within the range from 50 to 75 m^2. Capacity is referred to a unit of this surface area or, in specific terms, to unit area of pallet strand.

Finished sinter is crushed to lumps 70 to 100 mm across. Sinter is sized in screens with openings of 20 mm, and the fines (20 to 40% by mass) are returned to the feed.

The charge is composed of ore, coke breeze, dust and recycled materials. Ore is pre-crushed to 6-25 mm in hammer breakers and is generally not dried prior to sintering.

Porosity, gas permeability and greater surface contact area are the major advantages of sinter as compared to solid briquettes. The conversion from briquetting to sintering raised throughput capacity of blast furnaces and lowered fuel consumption. Fuel requirements in sintering amount generally to 8 to 10% of the mass of the charge.

Machine capacity in sintering of oxidized nickel ores in terms of sinter is 18 to 25 t/m^2 of strand area per 24 hours. Gases, carrying 0.2-0.3 g/m^3 of dust, are cleaned in cyclones.

In recent years, there has been a trend to agglomerate the charge by pelletizing in drums or pan pelletizers (Fig. 54). Prior to blending, the ore is ground to minus 5 mm. Additions of alabaster $2CaSO_4 \cdot H_2O$ or lime and subsequent drying make the pellets very strong. However, fine crushing and the frequently necessary drying are as yet costly.

Smelting Briquettes or Sinter

Blast furnaces for smelting oxidized nickel ores are similar in design to copper-smelting blast furnaces, but have a somewhat different cross-section profile (Fig. 47), suited to reducing smelting conditions and a rather deep hearth. Temperature in the tuyere zone attains 1450-1500°C, and at the furnace top, 300-500°C. The column of materials compo-

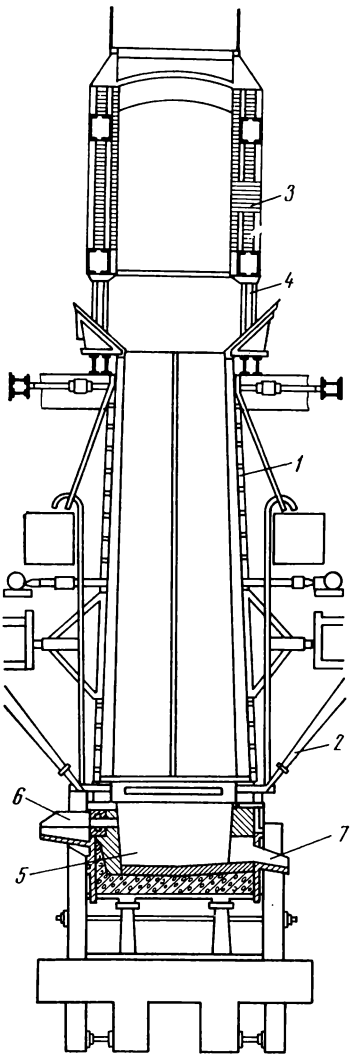


Fig. 47. Blast furnace for smelting oxidized nickel ores

1—water jackets; *2*—tuyeres; *3*—hood; *4*—charging ports; *5*—hearth; *6*—slag taphole; *7*—matte taphole

sed of sinter, pyrite (gypsum), fluxes and coke above the tuyeres is in a reducing atmosphere. Gases above the tuyeres in the centre of the furnace contain up to 35% CO, and at the top, up to 12-16% CO.

Owing to a high temperature and a reducing atmosphere, higher iron oxides are rapidly reduced to FeO (5-7).

Nickel is reduced but partly, as its content in the charge is low, while nickel compounds in sinter or briquettes are surrounded by gangue which prevents the access to reducing gases.

Melting begins by the formation of easy-melting mixtures in the system $FeO—SiO_2—CaO$, i.e., at a temperature of 1050-1150°C. Nickel silicates, iron protoxide and sulphide dissolve in the slag melt that trickles down.

Pyrite, if present in the charge, dissociates as the materials go down to give off vapours of elementary sulphur (56) even before the beginning of smelting.

Gypsum, only partly reduced to CaS at the surface of lumps, decomposes on contact with the primary silicate melt according to the reaction

$$2CaSO_4 + SiO_2 + 4CO \rightarrow$$

$$\rightarrow Ca_2SiO_4 + SO_2 + 4CO_2 \quad (123)$$

The evolving sulphurous gas is reduced to elemental sulphur and divalent sulphur compounds (reaction 84 and the following). Gaseous sulphur, carried by the stream of gases through the higher levels of the charge, is likely to be the chief sulphidizing agent of iron, and, through its intermediary, of nickel as well

$$2FeO + S_2 + 2CO \rightarrow 2FeS + 2CO_2 \quad (124)$$

$$6NiO + 4FeS + 2CO \rightarrow 2Ni_3S_2 + 4FeO + 2CO_2 \quad (125)$$

Direct sulphuration of iron and nickel by calcium sulphide is of secondary importance.

Next, an independent phase of matte, composed of Ni_3S_2 and FeS and dissolving free iron and nickel, separates from the slag melt. Relative amounts of sulphide and metal constituents of matte are governed by the ratio of metal sulphuration and reduction rates in smelting.

Matte saturated with free metals, when cooled, gives off solid solution crystals of nickel and iron, or ferronickel. Temperature in the tuyere zone is higher than in the hearth. As it comes to the hearth, the matte cools and ferronickel crystallizes on hearth bottom and walls. Accretions of ferronickel gradually build up in the hearth, its useful volume diminishes and furnace malfunction results. Ferronickel build-up can be prevented by adjusting smelting conditions in a manner to obtain mattes higher in sulphide and lesser in metal constituents.

Use of pyrite speeds up sulphuration. When pyrite is present in sufficient quantity, practically no ferronickel is formed in the hearth, but the excess iron sulphide makes the matte leaner. By contrast, excess gypsum affects but little matte composition as it has negligible effect on partial pressures of SO_2 and S_2 in the gases.

Slags contain 42-44% SiO_2 and about 50% of the aggregate of FeO, CaO and MgO. Generally high MgO content in the ore adds to reducing limestone consumption, as the CaO and MgO total in the slag should not exceed 36%. Nickel smelting slags can be used for casting paving blocks and manufacturing slag wool.

Furnace gases carry away up to 4-5% of the charge in the form of dust which is collected in settling chambers and

cyclones and returned to sintering. Gases are generally exhausted through a stack, although they can be used as fuel, if the furnace top is adequately sealed to prevent air entries.

Preheating of the air blast supplied to the furnace tuyeres and its enrichment in oxygen considerably improve blast furnace smelting performance, its capacity in the first place. Coke consumption is also lowered. Natural gas can be used to preheat the air blast.

Matte Converting

Nickel mattes are bessemerized in usual types of converters (Fig. 34).

Converting may be described by two main reactions, namely oxidation and slagging of iron and of iron sulphide (85) dissolved in matte

$$2Fe + O_2 + SiO_2 \rightarrow Fe_2SiO_4; \quad \Delta H = -575 \text{ kj (137 kcal)} \quad (126)$$

Transfer of a unit mass of iron to slag according to reaction (126) requires three times less air as compared to reaction (85). The rate of reaction (126) at the beginning of a blow through is much greater than that of reaction (85). In addition, iron can be oxidized by oxygen of the sulphurous anhydride:

$$3Fe + SO_2 \rightarrow 2FeO + FeS$$

Practice tends to indicate that iron sulphide is oxidized after the bulk of elemental iron is slagged off.

Nickel is oxidized very little until all of the iron is slagged off, since nickel protoxide, even if it would have been formed, would have converted to sulphide via the chief reaction of nickel smelting.

Matte is poured into a converter by ladles of 4 to 10-ton capacity and is each time blown through with quartz additions. Converter operations may be organized according to either an individual or a combined schedule. In the former, each converter operates individually, in the latter, a semiproduct from a number of converters is poured into one of them and treated to bessemer matte, while other converters re-start their cycle. Whatever the procedure, blowing is

continued to a point when the amount of molten mass in a converter corresponds to its capacity. Converter slag from these blows is relatively lean in nickel and cobalt as the matte in the converter still carries much iron. The duration of blowing through operations gradually increases, as matte accumulates in the converter, from 15 to 45 minutes because of a decrease in the ratio between the free and the sulphide iron.

When metallic iron is slagged, the converter tends to run hot and to counter this effect solid additions of ferro-nickel, solid matte and other nickel-bearing returns are charged into the converter to keep the temperature below 1350°C and so avoid rapid wear of the lining.

After a sufficient quantity of molten mass is accumulated in the converter, the copper-nickel matte forming stage is started. This stage is completed by skimming a final slag, rich in cobalt.

No nickel can be obtained from the converter nickel matte by further blowing in a converter as the reaction between nickel sulphide and protoxide

$$Ni_3S_2 + 4NiO = 7Ni + 2SO_2$$

can be carried out at high temperatures only (1600-1700°C) non attainable in a converter even with additional heating.

A converter slag contains 25-30% SiO_2, 42-48% Fe, about 1.5% Ni. Cobalt content in the bulk of slags is not more than 0.2%, but rises to 1.5% in the final skimmings.

Dust entrained with the gases through the converter mouth runs 15 to 20% Ni. It is collected in settling chambers and returned to converter in subsequent blows.

Converter nickel matte is cast into sand moulds, care being taken to prevent contamination by iron.

To recover cobalt, converter slags may be processed in a number of ways, depending on the subsequent flowsheet stages. If nickel of the converter nickel matte is extracted by electrolysis, it is advantageous to transfer cobalt to the converter nickel matte, and the procedure is identical to that in copper-nickel matte converting.

If nickel obtained subsequently from the converter nickel matte is not refined by electrolysis, cobalt is transferred to converter slags. The alternatives are: either to let cobalt

enter the final portions of the converter slag or, a more successful technique, to refine the converter slag by a special procedure. To this end, a small amount of fresh matte and quartz are fed to the converter before the end of a final blow.

The resultant increase in temperature favours transfer of cobalt to slag, which is skimmed after a 15-min blow. This procedure, repeated two or three times, allows an extraction of up to 80% Co to slags.

Cobalt-bearing slags are processed countercurrently in special heated converters or electric furnaces by a lean matte, and after enrichment in cobalt to 4-6% it is treated for recovery of the latter. Denuded slags contain mere 0.06% Co and 0.15% Ni and are dumped. The Ni-to-Co ratio by mass in the starting matte is about 30, and in the enriched mass, about 6.

Smelting Nickel from Nickel Matte

Converter nickel matte cast from the converter into moulds is crushed and ground after cooling, its subsequent processing depending on content of platinum metals and copper. If the former or the latter are in any appreciable quantities that call for electrolysis, processing of the converter nickel matte is similar to that described on page 210.

In the absence of platinum metals and in case of a moderate copper content, which allow the manufacture of grade H3 nickel without electrolysis, converter nickel matte requires special treatment.

After crushing and grinding to minus 0.5 mm, converter nickel matte is mixed with recycled dust and roasted in fluid-bed roasters at a temperature of about 1000°C to a calcine with 2-3% of residual sulphur.

The hot calcine discharged from the roaster at a temperature of about 700°C is passed through a non-heated reactor as a mixture with 10-15% of sylvinite (KCl + NaCl). In design the reactor is similar to rotary kilns (see Fig. 96).

The reactor cylinder, 12 m long and 1.6 m in diameter, is lined with fireclay brick in its leading half which is the site of chief processing reactions intended to transfer copper to water-soluble salts $CuSO_4$ and $CuCl_2$ (formation of the sulphate predominates).

The chemistry of the sulphating-chloridizing roast is not readily apparent, but it may be suggested that sulphurous gas from the oxidation of copper and nickel sulphides interacts with alkali metal chlorides, as,

$$2NaCl + SO_2 + O_2 \rightleftharpoons Na_2SO_4 + Cl_2$$

Next, in the presence of water vapours we have

$$Cl_2 + H_2O + SO_2 + CuO \rightleftarrows CuSO_4 + 2HCl$$

All these reactions give off heat with the effect that temperature rises to 750°C. In the trailing part of the reactor the charge cools down and after discharge it is leached by water, passing to the solution are $CuCl_2$, $CuSO_4$, Na_2SO_4 and residual alkali metal chlorides.

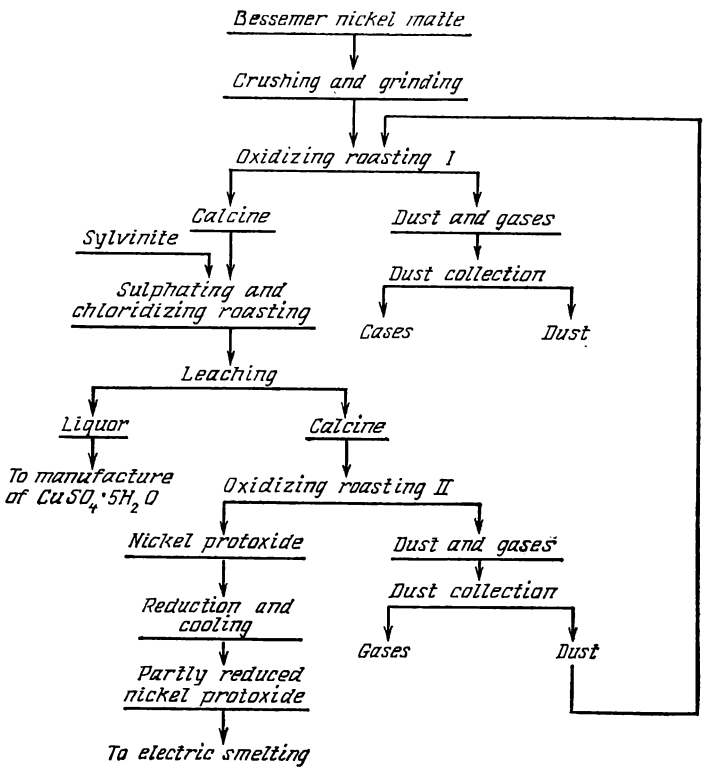


Fig. 48. Flowsheet for processing bessemer nickel matte to nickel grade H-3

Leaching is carried out by infiltration (percolation), and copper is displaced from the solution by scrap by a technique known as cementation.

Once copper is removed, the calcine carries not more than 0.45% Cu and it is treated for additional removal of sulphur in rotary kilns where sulphur content is brought down to about 0.02%.

The hot calcine of the second roast is mixed with 4-8% petroleum coke (used here because it carries no sulphur) and processed in a rotary cooler (14 m long, 1.6 m in diameter), similar in design to rotary kilns. In the leading lined half of the cooler, nickel protoxide is reduced partly at a temperature of about 700°C according to the reaction

$$NiO + CO \rightarrow Ni + CO_2$$

cooling taking place in the tail end which is sprayed with water on the outside.

Partial reduction of nickel with no fuel and electric power consumption is advantageous from the viewpoint of subsequent smelting.

Cooled burden is smelted in arc furnaces similarly to nickel protoxide that is obtained from copper-nickel mattes (page 210).

Metal is cast into moulds or poured in a thin jet into a water tank provided with a wire basket for discharging granules (small particles of irregular shape) of nickel. To avoid explosions, water is vigorously stirred. Granules are dried, packed into wooden casks and shipped to consumers. Granulated nickel is used for the manufacture of alloys. The flowsheet describing all the above processing stages is shown in Fig. 48.

Rotary apparatus, kilns and coolers, are frequently used for heating, cooling or processing various materials by gases. A loose material moves down a slightly sloped slowly rotating (1-2 rpm, slope of 1 or 2°) pipe, while hot combustion gases or cold air move in a countercurrent. The material may also be cooled by air or water blown and sprayed respectively on the outside surface of the pipe. Rotary apparatus are described in detail in Para. 47.

26. Electrolytic Refining of Nickel

Electrolytic refining is used to obtain nickel of higher grades (as specified by the USSR State Standard GOST 849-56, nickel grades H0, H1, H2) which should contain an aggregate of 99.8 to 99.99% Ni + Co and to recover noble metals, selenium, tellurium and cobalt.

Electrolysis is carried out in a solution of nickel sulphate or of a mixture of nickel sulphate and chloride with some electroconductive buffer additives.

The chief impurities in crude nickel are copper, iron, cobalt, silicon, platinum metals, sulphur, selenium and tellurium. When an anode of crude nickel dissolves, the only elements that pass in solution are iron, nickel, cobalt and partly copper.

The formation of ions Fe^{2+} and Co^{2+} requires no comment as their standard potentials are more negative than that of nickel, particularly so for lower concentrations in the

solution (Table 3). Partial solution of copper is the effect of concentration polarization. Sulphur bound with nickel may oxidize

$$S^{2-} - 2\bar{e} \rightleftarrows S^{\circ};\ E^{\circ} = -0.48 \qquad (127)$$

while that present in copper and silver sulphides precipitates with these compounds into anode mud. The remaining copper and all platinum metals settle out in the anode mud. Anode potential is too low to decompose water according to reaction (24). However, formation of metal oxides renders this possible. The anode then passivates, its dissolution slows down and instead there occurs a violent evolution of oxygen (the electrolyte as if boils). Addition of sodium chloride to the electrolyte prevents passivation of anodes.

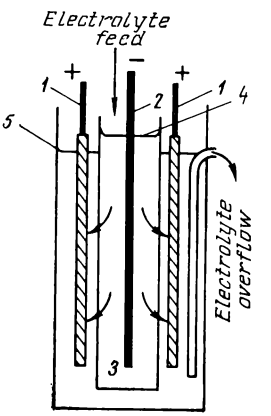


Fig. 49. Electrolytic cell for electrolysis of nickel
1—anodes; *2*—cathode; *3*—membrane; *4*—catholite; *5*—anolyte

At the cathode, the same electrochemical reactions should proceed in a reverse sequence, and here a primary discharge, first, of ions Cu^{2+}, then of hydrogen (Table 3) and, finally, of nickel and cobalt is to be expected.

To avoid deposition of copper, electrolytic cells are fitted with membranes, or porous partitions that separate anodes from cathodes. Membranes are made of synthetic fabrics based on lavsan and chlorine or of canvas. The fabrics are stretched over a framework of wooden laths. Each cathode is placed inside a membrane built as a flat box (Fig. 49).

The electrolyte inside the membrane is termed catholite and outside of it, anolyte.

Anolyte carries copper and other impurities, since ions of impurities are continuously dissolved in it from the anodes. Catholite should be free from impurities that may contaminate the cathode deposit.

Anolyte is continuously withdrawn from the cell and purified of impurities. A purified liquor is continuously

poured inside the membranes, its supply being adjusted in a manner to maintain the catholite level always about 50 mm above that of the anolyte. The effect of this is that catholite infiltrates through membrane pores and enters the anolyte space, while anolyte cannot pass through the membrane and so contaminate the catholite.

Anolyte Purification

Copper is removed from the anolyte by cementation with the aid of a specially prepared active nickel powder in conical cementation reactors (Para. 19) according to reaction

$$Cu^{2+} + Ni \rightarrow \downarrow Cu + Ni^{2+} \qquad (128)$$

A purified liquor carries less than 1-2 mg/lit Cu. Cement copper is treated by a special technique.

A freshly deposited nickel carbonate is added to the liquor, blown with steam and air, to neutralize excess acid according to the reaction

$$NiCO_3 + H_2SO_4 \rightarrow NiSO_4 + H_2O + CO_2$$

As pH rises, the rate of oxidation of divalent iron (Fe^{2+}) increases and it settles out as basic sulphates (101). Copper ions catalytically accelerate the oxidation of divalent iron, and this is why copper is removed after iron at some plants.

Iron is removed in pneumatic agitators (Para. 19), its content being brought down to 0.5-1.0 mg/lit after a 2-3 hours of stirring with nickel carbonate at 60-70°C. Nickel carbonate is prepared by precipitating nickel from a portion of the liquor by the action of soda ash.

Cobalt is removed by simultaneous action of gaseous chlorine and nickel carbonate

$$2Co^{2+} + Cl_2 + 3NiCO_3 + 3H_2O \rightarrow$$
$$\rightarrow \downarrow 2Co(OH)_3 + 3Ni^{2+} + 2Cl^- + 3CO_2 \qquad (129)$$

The deposit with 4-6% of cobalt hydroxide is treated for recovery of a part of nickel then transferred to cobalt extraction department.

Purified anolyte (less than 20 mg/lit Co) is suitable for supply inside the membranes and thus becomes catholite.

Electrolyte Composition Adjustment

A high current efficiency with relation to nickel requires to limit the concentration of hydrogen ions, or to raise pH of the electrolyte.

A pH of about 6 may cause $NiSO_4$ hydrolysis which is accompanied by a cathode settling of basic salts that make the metal deposit heterogeneous and scaly. To take this into account, the catholite of about pH-2.5 is supplied, and to avoid any raise in pH a buffer substance, boric acid, is added to the catholite.

Sodium sulphate and sodium chloride are introduced into the electrolyte to improve its electric conductivity, the latter substance also preventing the passivation of anodes. Compositions of anolyte and catholite are given in Table 19.

Table 19

Typical Compositions of Anolyte and Catholite in Nickel Electrolysis

Solution	Content, g/lit							
	H_3BO_3	Na^+	SO_4^{2-}	Cl^-	Ni	Cu	Fe	Co
Anolyte	5.0	30	110	50	65	0.60	0.50	0.50
Catholite	5.0	30	110	50	65	0.002	0.0019	0.020

Besides the solution of nickel, the anode is the site of oxidation of impurities and water. Current efficiency here is lower than that at the cathode, being generally close on 90%. This gradually lowers the concentration up by dissolving anode scrap, nickel powder or sulphide concentrate from converter nickel sulphide flotation. Anode scrap is dissolved in a sulphuric acid liquor in special cells with no membranes by passing an electric current. In the process copper settles out at the cathode and hydrogen evolves at the anode. Nickel powder and nickel concentrate are currently dissolved in titanium autoclaves in sulphuric acid under a pressure of oxygen according to reaction

$$Ni_3S_2 + 9O_2 + 2H_2SO_4 \rightarrow 6NiSO_4 + 2H_2O$$

Titanium is often used in the hydrometallurgy of nickel for protection against corrosion. Titanium is used to make starting sheets, autoclaves, fittings, parts of pumps and other apparatus.

Electrolytic cells (Fig. 50) are of concrete. They are lined with acid-resistant brick or ceramic tiles. Approximate dimensions of cells, in mm, are: length, 6000-6500; width, up to 1100; depth, about 1300.

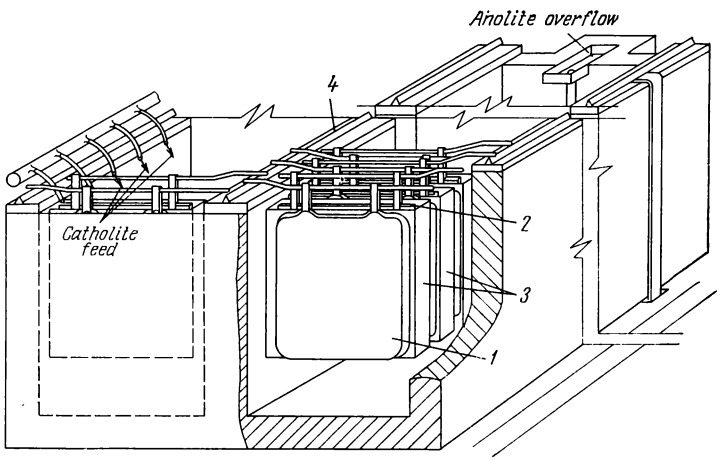


Fig. 50. Cell for electrolysis of nickel
1—anode; *2*—cathode; *3*—membrane; *4*—intermediate busbar

Anodes from crude nickel are cast as rectangular slabs of 200 to 250 kg whose size is 850 × 750 × 45 mm. Cathode starting sheets are by 50 mm wider and longer than the anodes and are manufactured by electrolysis with a purified electrolyte in separate starting sheet cells on sheets of stainless steel or titanium. A cell accommodates 30 to 45 cathodes and 31 to 46 anodes. Electrolysis is carried out at a temperature of 55-65°C and a current density of 225 to 350 A/m^2. Current efficiency with reference to nickel is 96% at a cell voltage of 2.4-2.5 V. Direct current power consumption varies from 2900 to 3300 kWh/t of nickel.

Nickel cathodes, 6 to 12 mm thick, are often not remelted to avoid contamination, but cut to small pieces and shipped to consumers.

The quantity of anode mud that settles to cell bottom is about 5% of the mass of anodes. It contains copper, nickel, sulphur, carbon, slag inclusions and platinum metals. The mud is dried, roasted and remelted into anodes for a secondary electrolysis. Secondary mud is higher in platinum metals and is shipped to gold-refining plants.

The importance of side recovery of platinum and its associates in nickel manufacture cannot be overrated, suffice it to state that some 30% of all the output of platinum and platinum-group metals in capitalist countries are obtained in the above manner.

27. Manufacture of Cobalt

In the processing of sulphide copper-nickel ores, cobalt, an associate of nickel, concentrates in the converter copper-nickel sulphide and in flotation passes predominantly to the nickel concentrate, then into anodes for electrolytic refining of nickel. When electrolyte is purified, cobalt is recovered as mud with 4-6% Co. The latter is dissolved in sulphuric acid in the presence of a reducing agent, e.g., according to the reaction

$$2Co(OH)_3 + SO_2 + H_2SO_4 \rightarrow 2CoSO_4 + 4H_2O \qquad (130)$$

Resultant liquors contain small amounts of iron, manganese, copper, nickel and other elements, and their treatment is dealt with below (see page 230).

In the processing of oxide nickel ores cobalt also associates with nickel. It is transferred from the converter nickel sulphide to a so-called anode mass which contains 8-10% Co, 58-64% Ni, 20-24% S (see page 220).

Anode mass is cast into anodes and treated by electrolysis in a NaCl solution (100-120 g/lit) in pairs with cast iron cathodes. At the anode, nickel, cobalt, iron and other metals go in solution as double-charge ions which hydrolyze directly and give a deposit of basic salts, "green hydrates",

whereas sulphur precipitates in elemental particles. Hydrogen evolves at the cast iron cathodes. Green hydrate deposit

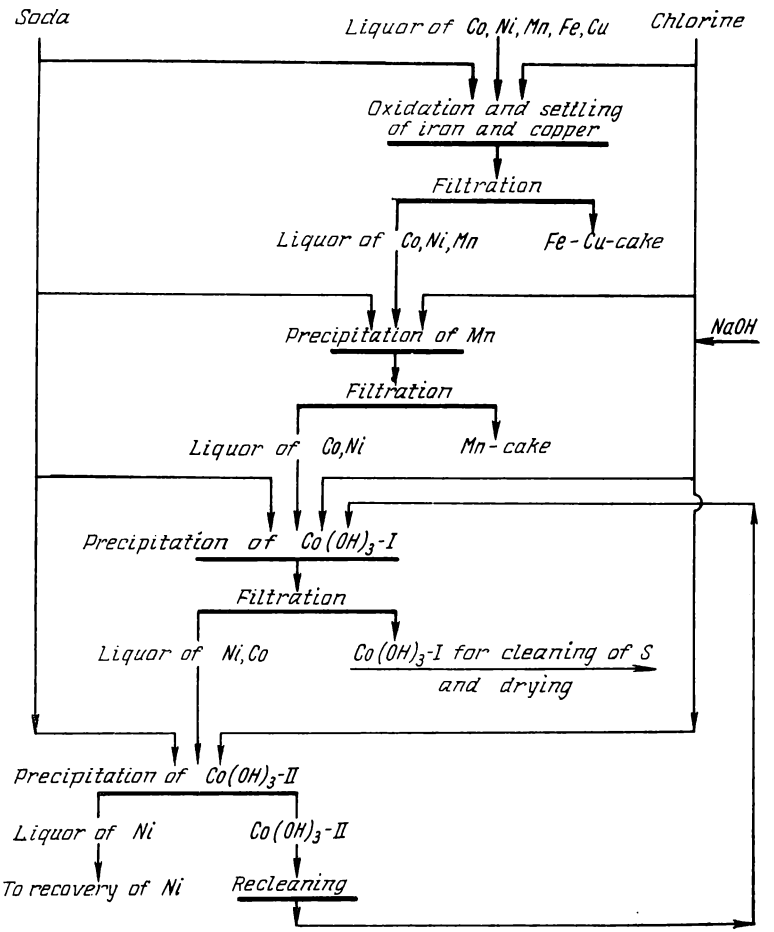


Fig. 51. Winning cobalt from cobalt liquors

is dissolved in sulphuric acid and filtrated from sulphur, the filtrate then being treated in subsequent processing stages. The above technique is complicated and costly because

of high consumption of electric power (4000 kWh/t) and of various other reagents, but is in use at some of the plants.

In the processing of zinc concentrates, cobalt, whose content is low, is gradually accumulated in the electrolyte to an admissible value and settled out at regular intervals from a part of the electrolyte as a xanthate cake which carries 4-5% Co and 0.5% Ni. The cakes are roasted, a first time to remove all organic matter, then a second time with a mixture of sulphuric acid to form sulphates. The product is leached with water, and cobalt passes in solution.

From pyrite concentrates which may contain 0.5% Co and 0.5% Cu, the balance, chiefly pyrite, cobalt is extracted by means of a sulphating-chloridizing roast with subsequent leaching of the calcine with water. The concentrates are roasted in a fluid-bed reactor with additions of sylvinite, attendant chemistry is similar to that described on page 220. Calcine is leached by infiltration in percolators.

Cobalt may also be extracted by many other techniques that are used for treatment of specific raw materials, both in the Soviet Union and other countries. All the above techniques, as the ones above, yield water liquors in which cobalt is often associated with predominant amounts of iron, nickel, manganese, copper and other elements. Liquors carry 5 to 10 times more nickel than cobalt, this requiring to extract nickel as nickel sulphate or other compounds.

A simplified flowsheet for winning cobalt from liquors is shown in Fig. 51. Iron is oxidized by chlorine and settled as basic salts by additions of limestone or soda, the deposit absorbing arsenic, antimony and bismuth impurities. Copper is extracted by a double substitution involving a cobalt or nickel powder, but may also be precipitated by soda. Manganese is eliminated by blowing the solution with chlorine or adding sodium hypochlorite NaOCl. As it is oxidized, manganese settles out as $MnO_2 \cdot H_2O$. From the purified solution that contains cobalt and nickel only, cobalt is settled out by chlorine or sodium hypochlorite according to reaction

$$2Co^{2+} + Cl_2 + 6H_2O = 2Co(OH)_3 + 2Cl^- + 6H^+$$

Simultaneous precipitation of nickel by a similar reaction is prevented by a substitution interaction in accordance with reaction (108).

Should nickel still pass to the deposited cobalt hydroxide, a fact liable to occur when Ni-to-Co ratio is high, the primary hydroxide is re-precipitated by the same technique after it is dissolved according to reaction (130).

The final hydroxide is mixed with soap, calcinated and washed with water for removal of sulphur as Na_2SO_4. After a second calcination, this time without soda, the resultant Co_3O_4 contains 70-72% Co, 0.2-0.3% Ni and hundredths of a per cent of other impurities.

Cobalt is smelted from the above oxide in electric furnaces in the presence of a low-sulphur reducing agent, refined by melting to remove carbon and sulphur, then cast into moulds.

Extra pure cobalt is obtained by electrolytical refining of the crude metal or by other methods.

Review Questions

1. What metals are associated with nickel in ores?
Cu, Au, Ag, Co, Bi, Zn, Pt, Cd.
2. Name chief techniques for dressing sulphide and oxide nickel ores.
Gravity concentration, magnetic separation, flotation, picking.
3. In what furnaces are nickel and copper-nickel mattes smelted from oxidized and sulphide ores?
Reverberatory, blast, electric furnaces.
4. What elements and compounds enter the composition of nickel and copper-nickel mattes?
Au, Cu, Ag, Pt, Ni_3S_2, Cu_2S, FeS, SiO_2, Al_2O_3, CaO.
5. What impurities are removed from anolyte in nickel electrolysis?
Cu, Pt, Co, Fe, Cl.
6. Place metals in a decreasing order of their affinities for oxygen and sulphur.
Co, Ni, Fe.

CHAPTER 4

METALLURGY OF LEAD

28. Chemical Properties of Lead

Lead is an element of group IV of the periodic table. Similarly to carbon, silicon, germanium and tin, it is capable of giving off four electrons. However, as it possesses a largest atomic number of the group, lead is more metallic in properties, while its oxides are amphoteric.

Lead is known from ancient times, as its use in fifth to the seventh millennia B. C. is now a well established fact. An early acquaintance of man with lead was favoured by the ease of reduction of the metal from ores, its low melting point and ductility which facilitated its working.

Natural lead of atomic mass of 207.21 is composed of four stable isotopes Pb^{204}, Pb^{206}, Pb^{207} and Pb^{208}. Owing to a relatively low boiling point, lead tends to vaporize in metallurgical processes as its vapour pressure even at 1000°C is about 133 N/m^2 (1 mm Hg)*; at 1170°C, 1330 N/m^2 (10 mm Hg); at 1500°C, 26 660 N/m^2 (200 mm Hg). Volatility is not only undesirable because of losses of metal with gases, but also hazardous due to the toxicity of vapours which bring about acute or chronic poisoning. Lead salts are toxic as well. It is assumed that a low mean life-span of ancient Romans, not higher than 32 was caused by chronic poisoning from extensive use of lead for the manufacture of kitchen ware and water pipes.

Lead is usually divalent. Compounds of this valency are for the major part salt-like. They dissociate with the formation of Pb^{2+} cation, however, plumbites, salts of metals in which the anion is PbO_2^{2-}, are not infrequent. Tetravalent lead derivatives plumbates with anions PbO_3^{2-}, PbO_4^{4-} and

* In accordance with the SI system of units, 1 mm Hg corresponds to 133 N/m^2.

other complex anions, are but rarely found in the field of metallurgy. Cation Pb^{4+}, which enters the composition of $PbCl_4$, $Pb(SO_4)_2$, and other salts is also known.

Because of a low negative value E^0 of the potential (high hydrogen overvoltage) lead is poorly soluble in hydrochloric, sulphuric and hydrofluoric acids. Its resistance to the action of these acids is further enhanced by surface films of $PbSO_4$, $PbCl_2$ or PbF whose solubility in water is low. Sulphuric acid in concentrations above 80% oxidizes lead, giving rise to a relatively readily soluble acid salt $Pb(HSO_4)_2$.

Corrosion resistance of lead to the action of acids, alkalis and many other compounds has promoted its wide use in the manufacture of or for the protection of chemical apparatus at the time when stainless steels and plastics were still unknown.

In the nitric acid lead dissolves vigorously according to reaction

$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

and what may be of interest, at a lesser rate in concentrated acid as compared to a slightly diluted one, because of a poor solubility of $Pb(NO_3)_2$ in a strong acid.

Oxidation of metal in the air at usual temperatures is prevented by a thin surface film of oxides. Molten lead at temperatures in excess of 500°C vigorously oxidizes to PbO, termed litharge. In molten alkalis, litharge dissolves to give plumbite

$$PbO + 2NaOH = Na_2PbO_2 + H_2O$$

When separated from metal lead, litharge is oxidized by air oxygen to Pb_3O_4 (minium) which is used for the manufacture of lead storage batteries, paints and putties; at temperatures higher than 550°C, minium decomposes

$$2Pb_3O_4 \rightarrow 6PbO + O_2$$

Lead dioxide PbO_2 is obtained through oxidation of minium by nitric acid and other oxidizers and by electrolysis of acid lead nitrate solutions. Lead dioxide is used in the manufacture of storage batteries and as a strong oxidizer in chemical syntheses.

Lead sulphide PbS, whose melting point is 1114°C, readily oxidizes in the air at temperatures in excess of 500°C to give sulphate, basic sulphate $PbSO_4 \cdot nPbO$ and oxide PbO.

Lead silicates are manufactured by melting together litharge and silica. Of these compounds, the most easy melting are $Pb_3Si_2O_7$ (705°C), Pb_2SiO_4 (740°C) and their mixtures.

Lead oxides and silicates can readily be reduced to metal by carbon monoxide at 600-700°C.

29. Source Materials for Manufacture of Lead. Dressing of Lead Ores

Lead is derived from ores and reclaimed lead. In ores it occurs in the form of various minerals, the major of which is lead glance, or galena PbS. Ores of oxide lead minerals, cerussite $PbCO_3$ and anglesite $PbSO_4$ are treated as well. However, the bulk of lead is obtained from sulphide ores.

Ores are generally of a complex variety, chief lead associates being zinc, copper and silver. Content of zinc often exceeds that of lead. Lead-zinc ores are chief raw materials for the manufacture of lead and zinc.

Zinc occurs in sulphide ores as sphalerite and wurtzite which are polymorphs of ZnS, also termed zinc blende, and as marmatite which is contaminated with iron. Iron occurs as pyrite FeS_2, less frequently as Fe_7S_8, while silver is represented mainly by argentite Ag_2S. In oxide ores, zinc is found as smithsonite $ZnCO_3$, while silver, as metal or AgCl, cerargyrite.

Copper is often present in lead-zinc ores in industrially valuable concentrations. In sulphide ores, as sulphides, and in oxide ores, as malachite and azurite.

Polymetallic ores often carry gold, silver, bismuth, antimony, arsenic, cadmium, tin, gallium, thallium, indium, germanium, selenium and tellurium.

Gangue of sulphide lead-zinc ores is composed of quartz, barite, calcite and small amounts of aluminium, iron, magnesium and calcium silicates. Ores occur in solid masses or as disseminated ores, contained most frequently in quartzites and siliceous shales.

Approximate compositions of lead-zinc ores are given below, %:

Pb	1.2	2.3	1.6
Zn	1.35	2.5	4.0
Cu	0.6	1.0	0.5
Fe	5.0	1.8	8.5
S	5.0	6.2	16.0

Necessity for a complex utilization of lead ores and a complexity of their composition have conditioned a wide use of flotation for their processing. Lead is no longer smelted directly from ores, as flotation allows enriching even the lowest ores, ones that contain a mere 0.3-0.5% Pb.

Flotation enrichment of lead-zinc or copper-lead-zinc ores involves the following steps. First separated is a bulk lead-copper concentrate, then a zinc concentrate and a pyrite concentrate follows in succession. Lead-copper concentrate is next divided by re-flotation into copper and lead concentrates. Pyrite concentrate is separated from these ores for the production of sulphuric acid or for the recovery of gold and silver, associated with pyrite. Sometimes direct selective flotation is more advantageous, when pulp is treated with various reagents to yield in succession a lead, a copper, a zinc and a pyrite concentrates.

Sulphide minerals of copper and lead are more amenable to flotation than sphalerite and pyrite. The former are floated in the froth by the action of small amounts of xanthate (a collector). In re-flotation, copper minerals are depressed by sodium cyanide, while galenite is floated to froth. NaCN adsorbed by the surface layers of copper minerals to coat them with films that accept no collectors, whereas galenite behaves differently and retains its flotability.

Sphalerite and pyrite are separated by carrying out the flotation in an alkali medium, in the presence of lime. Flotability of pyrite is then depressed, while sphalerite is activated by additions of copper sulphate.

Table 20 presents a tentative performance of a polymetallic ore flotation. It can readily be seen that the bulk of noble metals is distributed between copper and lead concentrates. A part of gold and silver is associated with pyrite, a fact which makes it imperative to separate the pyrite concentrate. If the copper concentrate is not separated in flotation,

noble metals generally pass to the copper-lead concentrate, their amounts in the zinc concentrate being relatively low. Another distinguishing feature is the predominant passage of bismuth to lead concentrates and that of cadmium to zinc concentrates, this being of a major importance for their subsequent recovery together with lead and zinc.

Table 20

Typical Performance of a Polymetallic Ore Flotation

Ore constituents	Yield, % of mass of ore	Cu	Pb	Zn	Au	Ag
		%			g/t	
Copper concentrate	9.44	27.8	2.3	4.86	3.67	163.0
Lead concentrate	1.41	3.7	47.2	14.5	6.6	73.4
Zinc concentrate	11.45	2.47	0.8	48.1	0.84	32.3
Pyrite concentrate	15.0	0.84	0.18	1.0	0.79	27.7
Tailings	62.7	0.1	0.1	0.98	0.01	0.005
Starting ore	100.0	3.14	1.08	6.96	0.72	37.0

Distribution of cadmium and disseminated elements among products of selective flotation of lead-zinc ores is shown in Table 21.

Table 21

Distribution of Cadmium and Disseminated Elements Among Products of Selective Flotation of Lead-Zinc Ores *, %

Elements	Concentrates				Tailings
	lead	copper	zinc	pyrite	
Cadmium	2-12	—	39.9-74.1	—	5-56
Indium	2-6	—	2.3-66.0	—	4-93
Thallium	7.1-100	—	Up to 5	Up to 12	Up to 90
Gallium	1.4-2	—	3.6-5.2	—	91-98
Germanium	Up to 20	—	—	—	74-98
Selenium	24	19	—	20	30-87
Tellurium	32	10	—	13	30-87

* According to data by M. A. Vinogradova, Tsvetnye Metally, 1959, No. 6, p. 39.

Cadmium, indium, thallium and germanium are mostly isomorphic with zinc blende, indium additionally with galenite, while selenium and tellurium predominantly with iron and copper sulphides. All these *disseminated* elements form no minerals of their own or are found in rarely occurring minerals, this fact underlying their generalizing name.

Lead concentrates from lead-zinc ores may be exemplified by a following composition, %: 39-78 Pb; 2-15 Zn; 0.3-4 Cu; 2-7 Fe; 14-20 S; 1-4 SiO_2; 0.3-2.3 CaO; 0.1-0.6 Al_2O_3.

Secondary raw materials are various lead and lead alloy scrap; up to 30% of all lead are now smelted from secondary raw materials.

30. Techniques for Smelting Lead from Concentrates

Reducing Smelting

A smelting technique that has found the most extensive use in lead manufacture is a reducing blast furnace smelting which is preceded by an oxidation sintering intended to turn sulphides into oxides and obtain the charge materials in the form of sinter.

Galenite is oxidized according to reaction (12).

Sinter is smelted together with coke to reduce lead

$$PbO + CO \rightarrow Pb + CO_2 \qquad (131)$$

Smelting conditions are adjusted by controlling the consumption of fuel and coke in a manner to reduce iron to FeO only and to transfer the latter to slag.

Impurities of a great affinity for oxygen are collected in the slag, while others are reduced to metals and become dissolved in lead. Resultant lead bullion, contaminated by impurities, is separated while molten from the lighter slag and transferred to refining units.

Reducing smelting is carried out in blast furnaces which require a lump feed, the way to solve the problem being sintering combined with roasting. Fluxes required in smelting are introduced into the sintering feed. A flowsheet for a lead reducing smelting is shown in Fig. 52.

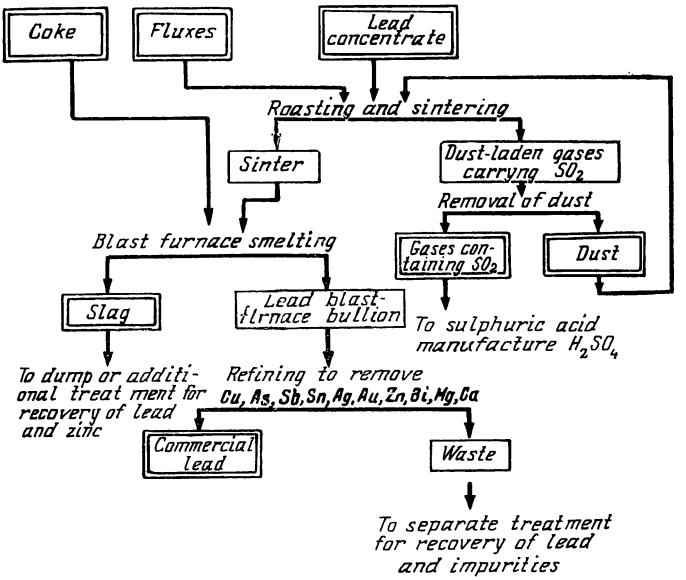


Fig. 52. Lead reducing smelting

Ore-Hearth Smelting

This technique known from ancient times is now used for the processing of very rich concentrates containing 75-78% Pb.

Air is injected into the charge composed of almost completely pure lead glance and lime. Lead sulphide oxidizes to PbO (12) and to $PbSO_4$

$$2PbO + 2SO_2 + O_2 \rightarrow 2PbSO_4 \qquad (132)$$

The oxidation is slow. The remaining sulphide interacts with oxide to yield lead

$$2PbO + PbS \rightarrow 2Pb + SO_2 \qquad (133)$$

The reactions are endothermic, $\Delta H > 0$, and to make up for the heat losses a small amount of fine coal or coke is added to the concentrate.

Ore-hearth smelting reactions are possible at temperatures as low as 700-800°C, which are insufficient for the melting of the charge which remains solid.

Droplets of reduced lead evolve from the loose charge incompletely, and besides, the reactions among sulphides and oxides are broken off because of the separation of the

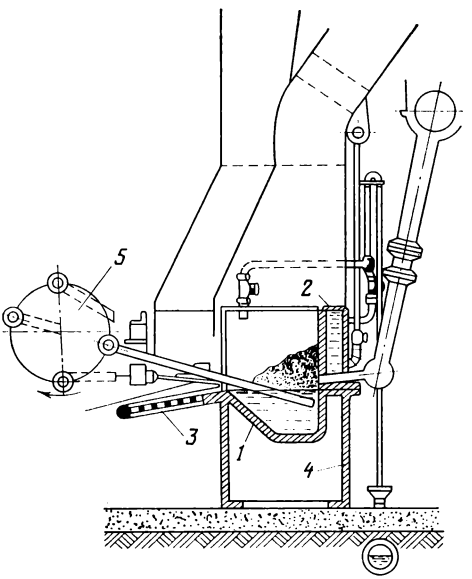


Fig. 53. Ore-hearth for smelting lead
1—basin; *2*—water jacket; *3*—apron plate; *4*—frame; *5*—rabbling mechanism

interacting substances by various impurities. Lead's extraction is but partial, and the process waste, grey slag, contains up to 30% Pb and requires additional treatment.

A hearth for lead smelting is shown in Fig. 53.

The basin is an elongated cast iron box about 2.4 m long, 0.5 m wide and 0.25 m deep with walls 50 mm thick. The hearth is placed on a brickwork or a steel frame. The furnace working space is enclosed on three sides by water jackets, and on the front, by a curtain of sheet steel that stops short of the basin and leaves a 500-mm opening above the basin which extends throughout the length of the front edge.

A cast iron apron plate with a runner along its outside edge adjoins the basin. The rear water jacket carries tuyeres arranged in line somewhat above the edge of the basin.

The hearth is started-up by heating the basin and filling it with molten lead. The charge, composed of lead concentrate, lime and fine coke or coal, is fed upon the surface of molten lead. The quantity of lime is 2-3% of the mass of the concentrate, and consumption of coal is 3-8% of the mass of the charge. Lead is pre-mixed with the concentrate.

The materials are charged in a manner to slope from the back wall to the front open edge of the bath. The tuyeres are underneath a layer of charge materials.

During smelting the charge is stirred by means of a rabble-arm actuated by a mechanism that slides along suspended tracks throughout the length of the front open edge of the basin. The end of the bar, that dips into the charge materials, moves in a vertical plane and simultaneously travels throughout the length of the hearth.

The melter who operates the hearth withdraws at regular intervals a portion of the charge materials onto the sloping cast iron plate and grades them by appearance. Poorly smelted charge is pushed back into the hearth, while gray slag is removed. Lead droplets that have separated in the process trickle into the runner on the outside edge of the plate.

Gases from the furnace working space are exhausted via a flue to dust catchers. An amount of dust carried away by the gases runs up to 25-30%, and, therefore, an adequate dust collection is essential to the ore-hearth smelting. Coarse dust settles in flues and settling chamber, while the finer sizes are collected in sleeve filters or electrostatic precipitators.

When 70 to 75% lead concentrates are processed, direct extraction to crude lead is 70%, while overall recovery, inclusive of the metal extracted in treatment of gray slag, is 95-97%.

The distribution of lead among ore-hearth smelting products may be described in the following terms: lead bullion, 65-70%; gray slag, 15%; dust, 15-20%. These data are conclusive evidence that as present-day standards go ore-hearth smelting is but an auxiliary treatment technique that allows a partial recovery of lead from rich concentrates in a single operation against small consumption of fuel and fluxes.

Hearth capacity is 6-10 t of concentrates in 24 hours per metre length of basin. Basins are not built in lengths greater than 2.5 m because of difficult servicing.

Reaction Smelting

A smelting technique, similar in chemistry to the ore-hearth method, is sometimes carried out in electric furnaces. The starting lead concentrate, with 65-70% Pb, is pelletized together with ground recycled sinter and dust. The pellets

are sintered in sintering machines at 800°C. Sinter which carries 5-6% S is smelted in electric furnaces at 1350°C. Up to 98% Pb are extracted to lead bullion and sublimates and 1.5% only is lost with slags. Because of a small consumption of fluxes the yield of slags is rather small, sublimates being recycled in sintering. Electric power consumption is about 600 kWh per ton of charge. The major advantages of this technique core considered to be its high smelting rate and improved working conditions as compared to the blast furnace or ore-hearth smelting.

31. Roasting and Sintering of Lead Concentrates

In order to obtain calcine as lump sinter that is suitable for a reducing blast furnace smelting, lead concentrates are roasted fused together with fluxes in sintering machines whose design is known from Para. 25.

Sulphides inflame on the surface of the charge from the action of igniter gases.Then, as the pallet cars move above the wind boxes, the underlying layers of the charge burn as well.

Oxidizing roasting in the sintering machines differs from that in multi-hearth furnaces by a greater speed of gas flow with respect to a relatively motionless charge and relatively high temperatures inside the body of materials.

The chief sources of heat are oxidation of PbS (12), $\Delta H = -840$ kj (−200 kcal), and of pyrite (69), $\Delta H = -3310$ kj (−792) kcal).

Zinc blende, of which there is little in the charge, oxidizes according to the reaction

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2; \qquad \Delta H = -880 \text{ kj } (-210 \text{ kcal}) \tag{134}$$

Oxidation of such impurities as arsenopyrite (72) and other arsenic sulphides, as well as of antimonite Sb_2S_3 results chiefly in readily volatile trioxides, as,

$$2Sb_2S_3 + 11O_2 \rightarrow 2Sb_2O_3 + 6SO_2 \tag{135}$$

Formation of higher oxides of these elements and of sulphur trioxide according to reaction (18) is enhanced

by their bonding with lead oxide into stable arsenates, antimonates and sulphates.

Oxides of lead, cadmium, sulphides of lead, antimony, tin and metallic lead possess appreciable vapour pressures (see Table 22) at sintering temperatures. They evaporate partly and are carried away by gases.

Table 22

Approximate Data on Volatility of Some Metals and Their Compounds

Metals and compounds	Vapour pressure, N/m^2 (mm Hg), at temperatures, °C	
	750—850	1000—1100
Lead	3.5 (2.6·10⁻²)	666.5-799.8 (5-6)
Lead oxide	13.3 (0.1)	533.2-1999.5 (4-15)
Lead sulphide	266.6 (2.0)	2266.1 (17.0)
Antimonous sulphide	1200 (9.0)	17 329 (130)
Arsenic trioxide	10 131 (760)	—

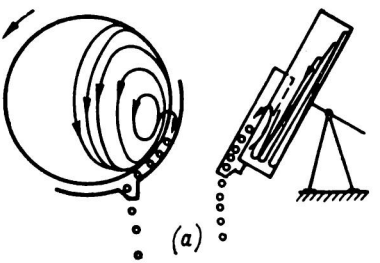
The charge sinters because of the formation of readily melting compounds and alloys. Lead silicates and their alloys melt in the range from 670 to 883°C. Eutectics in the system SiO_2 — FeO — CaO soften at 1030-1050°C, and sulphides and their mixtures, do so within the temperature interval between 800 and 1100°C.

An early sintering is objectionable as the easy-melting constituents may coat the still unoxidized sulphide particles, preventing all access of air to their surface, with the effect that unoxidized sulphur will remain in the sinter. However, adequate decomposition of sulphates and agglomeration sintering should be completed at 1000-1100°C.

Premature sintering of charge materials can be prevented by mixing the concentrate with ground fluxes (in amounts required for the subsequent melting) and returns (fine sinter unsuitable for smelting) which separate the easy-fusing concentrate particles. Besides, the limestone that is intro-

duced into the charge dissociates in sintering to CaO and CO_2 with an absorption of heat, thus preventing a sharp increase in temperature. A similar temperature control at ignition is exerted by water which is sprayed on the charge materials before they are fed to the sintering machine.

Moistening to 8-10% promotes sticking of concentrate particles into small balls which form a less compact bed



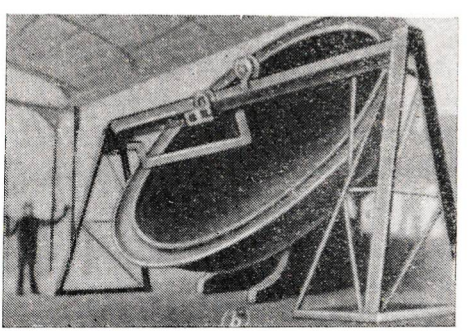


Fig. 54. Pan pelletizer
a—pelletizing diagram; *b*—general view of pan pelletizer

than a powder and prevent dust formation when charge materials are fed to the machine. The charge is blended with 2 or 3 parts of the previously formed fine sinter, unsuitable for smelting because of its fineness, or it is roasted twice (double sintering). The choice of the technique is governed by the composition of raw materials and local conditions. The amount of sulphur, burned per 1 m^2 of sinte-

ring pen conveyor in 24 hours is practically unaffected, lying between 0.7 and 1.2 t.

Pelletizing (agglomeration) gained a wide recognition industrially in processing of powder materials. A humidified powder material is mixed by tumbling in a slowly rotating drum (barrel) or on the bottom of an inclined rotating pan. In the process, the material balls up or pelletizes to spheroid pellets (balls) up to 20 mm in diameter. In many instances, it is more advantageous to roast pellets than powder in sintering machines. A pan pelletizer is shown in Fig. 54. A 4.2-m dia pan has a capacity of 20 to 50 t/h.

Lead concentrates particles are for the most part finer than 0.1 mm. A similar fine grinding of fluxes and recycled sinter would have promoted greater homogeneity of the charge, but this would have lowered its gas permeability and increased processing costs. Therefore, fluxes are ground down to 6 mm, and recycled sinter down to 8 mm. Fluxes are crushed in jaw and cone crushers, and sinter, in roll breakers.

The charge is fed to the sintering machine by an apron feeder via a humidifier from which the materials are discharged to a pendulum feeder that oscillates in a plane at right angle to the machine longitudinal axis (Fig. 55).

The pendulum feeder spreads the charge over the width of the pallet car, and as the latter moves the charge is levelled by a fixed blade. Bed thickness is governed by gas permeability of the charge and lies between 200 and 300 mm.

The degree of oxidation of sulphides depends on the time the car resides above the suction boxes, its travel speed being 0.6-1.5 m/min. Sulphide oxidation rate and the temperature inside the bed of materials are affected by the quantity of air being sucked and can be adjusted by varying the vacuum inside the suction boxes.

Sintering gases contain SO_2, vapours of volatile compounds and dust. Dust is collected in dust catchers, and clean gases may be used for the manufacture of sulphuric acid, but only when their SO_2 content is above 4%. A most concentrated gas is obtained at the beginning of sintering, in the first few suction boxes. As sulphur oxidizes, SO_2 percentage falls off. To minimize the effect of dilution, the

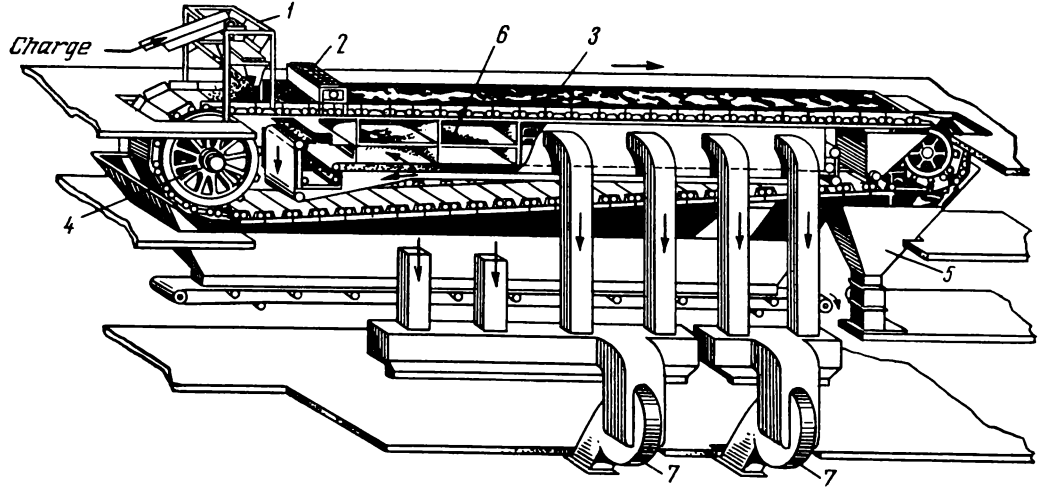


Fig. 55. Sintering machine

1—feed hopper; *2*—ignition furnace; *3*—charge bed on pallet cars; *4*—driving sprockets; *5*—sinter hopper; *6*—suction boxes; *7*—fans

suction box is compartmented. A frequent practice is recycling of lean gases and their repeated suction through the charge bed.

In recent time, much attention is being given to up-draft sintering. In this technique, suction boxes become blast-distribution boxes, a pressure, not a vacuum being provided inside them. The blast permeates the bed of charge from below upwards. This technique prevents rapid disintegration of pallet car grating and facilitates recycling of sintering gases (Fig. 56).

In the metallurgy of lead dust is often collected, in bag filters which are sleeves 160-220 mm in diameter and 2.8 to 3.5 m long, of cotton, wool, synthetic fabric or glassfibre. Bag filters operate on the principle of filtration of dust-laden gas through the fabric.

A schematic diagram illustrating bag filter design is given in Fig. 57. Dust-laden gas arrives along a pipe underneath a horizontal partition provided with branch pipes for gas-tight fastening of the open ends of sleeves. Closed ends of bags are suspended to a frame connected to vibrating mechanism. Gas is sucked through the fabric by a fan, the dust remaining on the inside surface of the sleeves. The frame that supports upper ends of sleeves is vibrated at regular intervals by mechanisms *5*. In the process, gate *6* closes automatically, and the gas motion ceases. Dust that has settled inside the bags falls from them into underlying bins and is discharged by screw conveyor *7*.

Bag filter dust collection efficiency may be as high as 90%, running costs being low. A shortcoming of this type of filters is a low capacity, which is mere 1-2.5 m^3 per square metre per minute.

Bag filters for cleaning large quantities of gases would have been quite bulky, and, therefore, they find chief application in small-scale manufactures. In particular, they are widely used in the metallurgy of lead where the amounts of treated gases are relatively small.

The temperature of gases entering the dust collectors should not exceed 100°C otherwise the bags are likely to be damaged. At the same time, gases should be heated above the water vapour dew point, as condensation of water on the surface of bags blocks fibre pores. Bags of nitron, glass-

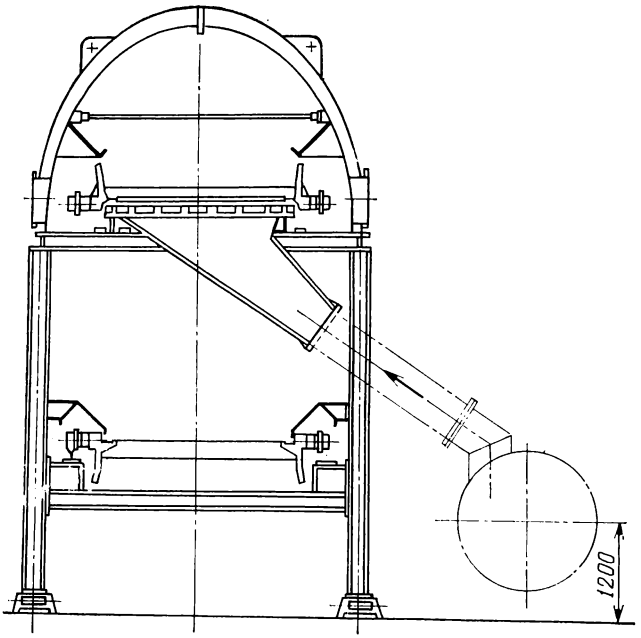


Fig. 56. Up-draft sintering machine

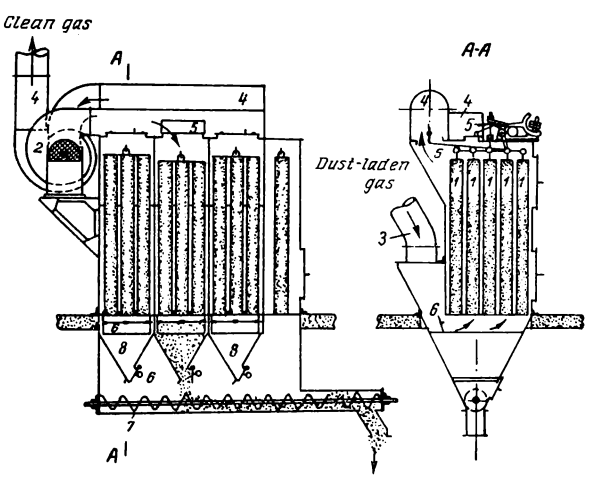


Fig. 57. Bag filter

1—sleeves bags; *2*—exhaust fan; *3*, *4*—flues; *5*—vibrating mechanism; *6*—gate; *7*—dust screw conveyor; *8*—dust hopper

fibre and lavsan are more heat-resistant (respectively 130, 150 and 250°C), but they are more expensive.

Bags may be cleaned of dust not only by mechanical vibration, but by air blown in the reverse direction to normal gas flow. To this end, a number of sections are disconnected from the common gas handling system and cleaned with air flow in a reverse direction to remove dust that has infiltrated inside the pores.

In modern practice, bag filters are preferably replaced by electrostatic precipitators which are of a greater efficiency although their collection ability with respect to lead and zinc oxide particles is lower.

32. Lead Bullion Smelting

Smelting Procedure

Sinter is smelted in blast furnaces similar to those for smelting copper or oxide nickel ores. Furnaces are provided with an internal hearth from refractory brick on a concrete foundation in the form of a trough about 600 mm deep. Hearth fireclay walls are faced internally with magnesite brick, the brickwork being reinforced by a steel casing and a framework of steel beams (Fig. 58).

Lead is tapped continuously through a siphon, a canal 250 × 250 mm in cross-section. One end of the canal enters the hearth at the furnace bottom, while the other end opens into a flat dish with a discharge spout. After the hearth is filled, excess quantity of lead flows from the siphon to the dish and then to a ladle. Should the siphon be plugged, metal can be tapped through holes located at the bottom. The siphon adjoins the middle of one of the longer sides of the hearth. Modern large-capacity furnaces are provided with two siphons spaced 2 m apart.

Water jackets are similar to those of copper smelting blast furnaces, but they are of a lesser height and arranged in two rows, one above the other. Bottom water jackets that rest on the hearth are sloped 5-7 degrees to the inside. End-face water jackets are vertical and have openings for accommodating the tapping water jackets which are iron plates with cast-in coiled pipes and slag and matte tap holes.

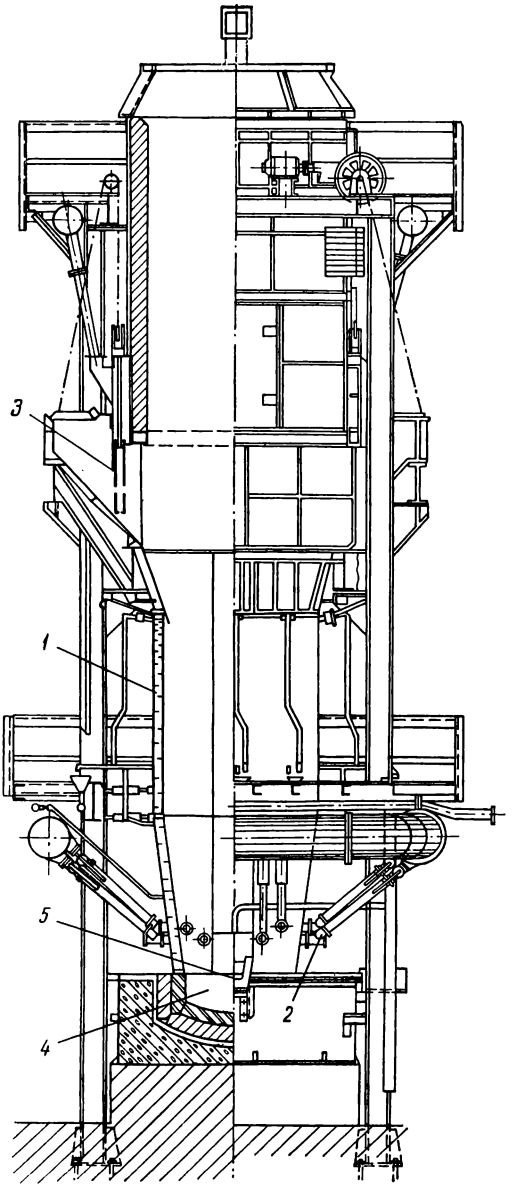


Fig. 58. Blast furnace for smelting lead

1—water jackets; *2*—tuyeres; *3*—charging ports; *4*—hearth; *5*—taphole for discharge of matte and slag

The tuyeres are arranged similarly to the copper smelting blast furnaces and their diameter ranges usually from 100 to 125 mm.

The furnace top arrangements for charging materials and exhausting gases are of a gas-tight design to improve sanitary conditions.

Lead smelting blast furnaces are up to 8 m long. At tuyere level they are 1.4 to 1.6 m in dia, and their height from the tuyeres to the furnace top is 5 to 6 m.

The furnace is charged with coke and sinter that carries fluxes necessary for slagging. An alternative practice is to charge fluxes (gold-bearing ones preferably) directly into the furnace, thus obviating the need for costly grinding.

The bulk of the charge is less than 100 mm in size. Content of fines (lumps less than 25 mm) should not exceed 10 to 15%. Charging rate is governed by the descent of the column of materials, its level at the furnace top being maintained constant.

Most of coke burns in the tuyere zone, the temperature there reaching 1400-1500°C and even 1550°C in separate sections. Combustion products flow upwards, permeate the charge and give it its sensible heat. Temperature inside the hearth is lower (900-1200°C) than in the tuyere zone. The temperature of waste gases at the furnace top is 150-200°C.

Composition of gas gradually changes along the height of the furnace. Coke burns to CO_2 at the tuyere level. As the carbon dioxide ascends with other gases to higher levels of incandescent coke, it is converted to carbon monoxide. As the gases move further up, CO content falls off, while that of CO_2 rises, chiefly because of the reduction of metal oxides.

Still in sintering a part of lead is bound into silicates having a melting point of about 700°C. Soon after charging into the blast furnace, silicates begin to melt and dissolve oxides of other metals. Therefore, oxides of lead, iron and other metals are reduced in blast furnace smelting chiefly from a silicate melt that trickles down countercurrently to the stream of hot reducing gases.

The affinity of iron for oxygen is much greater than that of lead. In smelting, the temperature and the CO concentra-

tion can be maintained at such values that would cause a practically complete reduction of lead and allow iron as FeO to pass over to slag.

When iron is reduced in part only, lead is not contaminated, since iron is insoluble in molten lead. Despite this fact, steps are taken not to reduce iron, since it causes build-up of accretions, which hamper furnace operation, and a slag low in ferrous oxide content loses some of its essential properties.

Contaminating copper, bismuth, antimony, arsenic and other metals are reduced simultaneously with lead and dissolved in molten lead.

Lead, copper and iron sulphides that have not oxidized in roasting, melt together to give mattes of melting points between 950 and 1100°C. Irrespective of what metals sulphur is bound with in the sinter, those metals pass to matte, whose differences of affinities for sulphur and oxygen are the greatest, namely, copper, lead and iron. The final composition of the matte is the effect of its interaction with slags and lead bullion

$$(Cu_2O) + [FeS] \rightarrow [Cu_2S] + (FeO) \qquad (136)$$

$$2\{Cu\} + [PbS] \rightarrow [Cu_2S] + \{Pb\}^* \qquad (137)$$

Sulphates of lead, zinc and other metals are reduced to sulphides, i.e.,

$$PbSO_4 + 2C \rightarrow PbS + 2CO_2 \qquad (138)$$

$$ZnSO_4 + 2C \rightarrow ZnS + 2CO_2 \qquad (139)$$

Decomposition of sulphates through interaction with silica or silicates is also possible

$$PbSO_4 + SiO_2 + CO \rightarrow PbSiO_3 + SO_2 + CO_2 \qquad (140)$$

$$ZnSO_4 + SiO_2 + CO \rightarrow ZnSiO_3 + SO_2 + CO_2 \qquad (141)$$

Practice shows that reduction of sulphates proceeds at a faster rate than their decomposition, and, therefore,

---

* Here, as before, enclosed in round brackets are concentrations in slag, in square brackets — in matte; and in fancy brackets — in crude metal.

desulphurization in lead smelting generally lies between 20 and 40%, the remaining sulphur passing to matte.

Lead smelting mattes have a density of 4800 to 5200 kg/m^3. In the hearth, they form a molten layer of their own, located between the lead and slag.

Noble metals in a sinter are in elemental state (silver may be found additionally as Ag_2S). Molten lead and matte are good solvents for gold and silver, and the noble metals concentrate in these smelting products. Recovery of gold, silver and lead from mattes necessitates additional treatments involving losses of metals and costs. Therefore, formation of mattes is undesirable and may be justified in smelting of cupriferous concentrates. If such a concentrate were roasted to a complete elimination of sulphur, copper would have been reduced to metal in smelting and dissolved in lead. In the furnace hearth, where the temperature is lower than that at the tuyeres, copper may settle out and plug the siphon and give wall accretions in the hearth, gradually decreasing latter's capacity. This possibility is minimized by leaving sulphur in the sinter in amounts sufficient to form mattes. In this case, most of the copper passes in smelting to matte and no accretions appear in the hearth.

In lead smelting, zinc oxide is reduced to metal whose vapours are entrained by gases and re-oxidized. Some of zinc oxide dissolves in slag. Zinc sulphide is distributed between matte and slag. Zinc sulphide is poorly soluble in slag and is found in the latter as a suspension that increases slag's viscosity. For this reason, it is good practice to roast dead (until complete elimination of sulphur) zinciferous concentrates.

When both copper and zinc are present, a dead roast is also to be preferred as zinc is a greater smelting risk than copper whose crystallization can be countered by increasing the temperature inside the hearth.

The yield of matte in lead smelting is rather small. Separate tapping of matte is difficult because of a small thickness of layer, and, therefore, slag and matte are tapped together into the heated forehearth. As matte accumulates, it is withdrawn from the forehearth through tapholes and treated by a separate process. Approximate matte composi-

tions are given below, %:

Cu	10.2	19.5	28.8	35.0
Fe	48.8	37.1	19.8	15.0
Pb	7.8	11.6	17.7	15.0
Zn	5.4	5.5	7.0	7.0
S	23.0	21.7	20.0	20.0
Ag, g/t	—	700	—	1000

Furnace gases above the column of charge materials carry much carbon monoxide, but generally they are diluted with air and are not suitable as fuel.

Dust entrained by gases settles partly inside flues, while its finer fractions are collected in electrostatic precipitators or bag filters. Dust from flues is recycled to roasting charge. Cadmium and disseminated metals, whose volatile compound vapours are carried out of the furnace by gases, concentrate in the finer dusts, which are processed separately after collection to recover various values.

Given below are compositions of dust collected from lead smelting gases by electrostatic precipitators and bag filters, %:

Cd	0.40	1.57	2.30
Pb	77.8	63.83	57.58
Zn	2.51	13.20	8.80
As	0.045	0.34	0.54

A most valuable dust constituent is cadmium, its recovery requiring a special treatment.

Slags that meet lead smelting conditions should melt on the interval between 1150 and 1200°C. Excessively fusible slags trickle at too fast a rate into the hearth so that their lead oxide is reduced but incompletely. If slags are excessively high-melting, overconsumption of fuel is unavoidable.

The chief purpose of slag is to bind and eliminate from the furnace iron oxides and silica. However, slags including too much FeO have too high a density and their separation from mattes is poor. Besides Fe_2SiO_4 that is low-melting carries much FeO, a fact which promotes reduction of iron to metal in the process of smelting.

Calcium oxide lowers slag density and enhances reduction of lead by substituting for it in silicates, since the affinity of calcium oxide for silica is much greater than that of lead oxide

$$PbSiO_3 + CaO + CO \rightarrow Pb + CaSiO_3 + CO_2 \qquad (142)$$

When materials high in zinc are smelted, account should be taken of the fact that slag dissolves much zinc oxide, whose solubility increases with higher FeO content and falls off with higher SiO_2 and CaO contents.

Given below are compositions of slags most suitable for the smelting of zinciferous charges, %:

SiO_2	30.6	23.5	19.8	16.3
FeO	38.3	39.2	39.9	40.1
CaO	16.1	12.3	9.9	8.6
ZnO	5.0	15.0	20.0	25.0

Slags contain from 0.9 to 1.5% lead and from 0.2 to 1.0% copper. Part of lead is present as unsettled droplets of metal and matte, and, therefore, it is good practice to settle slags in heated settlers, where the slags are averaged in the process of their accumulation before further treatment. Settlers are similar in design to electric furnaces and are equipped with three carbon electrodes that pass through the roof and dip into the slag melt. Electric current flowing through the layer of slag overheats it, enhancing the settling of values.

Volatilization of Lead and Zinc from Slags

Lead and zinc, dissolved and dispersed as matte and metal in slag can be recovered by volatilization in a slag-fuming furnace (Fig. 59) which is built of water-cooled jackets resting on a cast iron plate. The furnace measures 3×7 m in plan and is up to 10 m high. The longer sides of furnaces carry 11 to 36 tuyeres up to 100 mm in diameter. Slag is poured to some level above the tuyeres, and pulverized coal, serving both as fuel and reducer, is injected into the furnace via tuyeres. CO from combustion of coal inside floating gas bubbles reduces zinc and lead oxides of the slag. Coal particles, which float up in the slag chiefly with the aid of gas bubbles formed of a mixture of CO and CO_2 that attach themselves to the particles, also participate in the reduction.

At a temperature of about 1300°C reduced metals and lead sulphide volatilize. Their vapours, carried to the slag surface, are oxidized and entrained by gases as fine dust with 15 to 25% PbO and 60 to 75% ZnO. Gases are cooled,

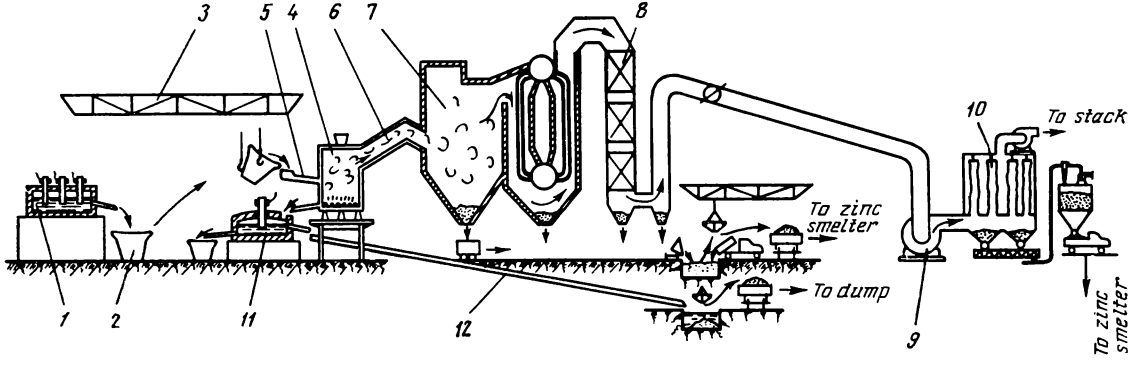


Fig. 59. Volatilization of lead and zinc from slags

1—electrically heated settler; *2*—slag ladle; *3*—overhead crane; *4*—slag-fuming furnace; *5*—runner for pouring slag; *6*—flue; *7*—chamber for burning of CO and steam boiler; *8*—air heater; *9*—fan; *10*—sleeve filter; *11*—electrically heated settler; *12*—runner to slag granulation pit

their sensible heat being recuperated in waste-heat boilers and air heaters, and dust is finally collected in sleeve filters. After the slag is blown (fumed), it is good practice to settle it once more in a heated settler.

This technique allows a recovery from slag of up to 90% Zn and 95 to 98% Pb. Dust is processed in zinc manufactures.

Slag-fuming furnaces are batch apparatus that process 40-50 t of slag at a time over a period of about 2 hours. Coal consumption averages 20% of the mass of the slag.

Lead Smelting Performance

Capacity (smelting power) of lead smelting blast furnaces varies from 40 to 80 t/m^2 per 24 hours depending on charge composition and quality of sinter. Homogeneous as to size and strong sinter is readily permeable to gases, this promoting uniform combustion of fuel and improving its efficiency. These conditions also govern the combustion of costly fuel, coke, whose consumption varies from 8 to 17% of the mass of the charge. Coke consumption may be brought down by heating air in recuperators which burn natural gas and by enriching air in oxygen. Oxygenation of blast to about 26% of oxygen reduces coke consumption by 10-15%, increases furnace smelting power by 25% and brings down dust entrainment by 20-25%.

Recovery of lead to lead bullion is governed by charge composition, fall of side products and processing techniques involved. Concentrates contaminated with small amounts of copper and zinc allow a recovery of Pb and noble metals of 95%, recovery falling off to about 90%, if content of copper and zinc is high.

Lead Reducing Smelting Charge Calculations

Calculate a charge for roasting and smelting a concentrate containing 50% Pb, 12% Zn, 3.1% Cu, 20% S, 2% SiO_2, 6.5% Fe and 3% CaO.

The available fluxes are materials listed in Table 23.

From practical data on smelting of similar concentrates,

Table 23

Composition of Fluxes

Material	Content of, %		
	SiO_2	Fe	CaO
Iron ore	10.0	60.0	2.0
Gold-bearing quartz	80.0	10.0	1.0
Limestone	7.0	5.0	50.0

matte composition is assumed to be as follows: 29% Cu; 18% Pb; 7% Zn; 20% S; 20% Fe.

Recovery of copper to matte is about 80%. Amount of copper entering matte from 100 kg of concentrate is

$$3.1 \cdot 0.8 = 2.5 \text{ kg}$$

The quantity of resultant matte is

$$\frac{2.5}{29} \cdot 100 = 8.6 \text{ kg}$$

Amount of sulphur in the matte is

$$8.6 \cdot 0.20 = 1.7 \text{ kg}$$

If desulphuration in smelting is assumed equal to 20%, the necessary amount of sulphur in the sinter is

$$\frac{1.7 \cdot 100}{80} = 2.1 \text{ kg}$$

Desulphuration in sintering is

$$\frac{20 - 2.1}{20} \cdot 100 = 89.5\%$$

Zinc in sintering and smelting distributes itself between slag, matte and gases. Let us assume that 80% of Zn enters slag, i.e., $12 \cdot 0.8 = 9.6$ kg (12.0 kg in terms of ZnO).

Amount of iron to be slagged (minus the amount going to matte) is

$$6.5 - 0.20 \cdot 8.6 = 4.8 \text{ kg}$$

The quantity of zinc that passes to slag is much greater than that of iron, SiO_2 and CaO. To form a slag capable of

dissolving zinc oxide, it is necessary to introduce all the three fluxes.

Of the slags given in page 253, we choose the following composition: 20% ZnO, 20% SiO_2, 31% Fe, 10% CaO (in rounded off figures).

The yield of slag, calculated on the basis of dissolved zinc oxide, will be

$$\frac{12}{20} \cdot 100 = 60 \text{ kg}$$

Denoting by x, y and z the quantities of iron, quartz and limestone respectively, we set up the equation of charge balance:

	Amount to be slagged, kg	In iron ore, kg	In quartz, kg	In limestone, kg	In slag, kg
Fe	4.8	$+ 0.6x$	$+ 0.1y$	$+ 0.05z$	$= 60 \cdot 0.31$
SiO_2 . . .	2.0	$+ 0.1x$	$+ 0.8y$	$+ 0.07z$	$= 60 \cdot 0.2$
CaO . . .	3.0	$+ 0.02x$	$+ 0.01y$	$+ 0.50z$	$= 60 \cdot 0.1$

After multiplication by 100 and conversion, we obtain

$$\begin{aligned} 60x + 10y + 5z &= 1380, \\ 10x + 80y + 7z &= 1000, \\ 2x + y + 50z &= 300 \end{aligned}$$

The solution of the system of equations will give us

$$x = 21.5; \quad y = 9.4; \quad z = 5.0$$

To verify the calculation, we draw up a charge balance sheet, as shown in Table 11.

33. Lead Bullion Refining

Lead bullion is generally of a following composition, %: 96-99 Pb; 0.05-2.4 Cu; up to 0.45 As; 0.6-0.9 Sb; up to 0.2 Sn; 0.005-0.07 Bi; up to 0.6 Ag.

The USSR State Standard GOST 3778-65 specifies six grades of lead bullion*, containing lead in quantities not less than, %: C0, 99.992; C1, 99.985; C2, 99.95; C3, 99.9.

* Inclusive of extra-pure lead: C000, 99.99954% Pb, and C00, 99.99852% Pb.

The purpose of refining is to remove impurities and increase lead content to the specified standard level. In the process of refining, copper, noble metals, bismuth, arsenic, tin

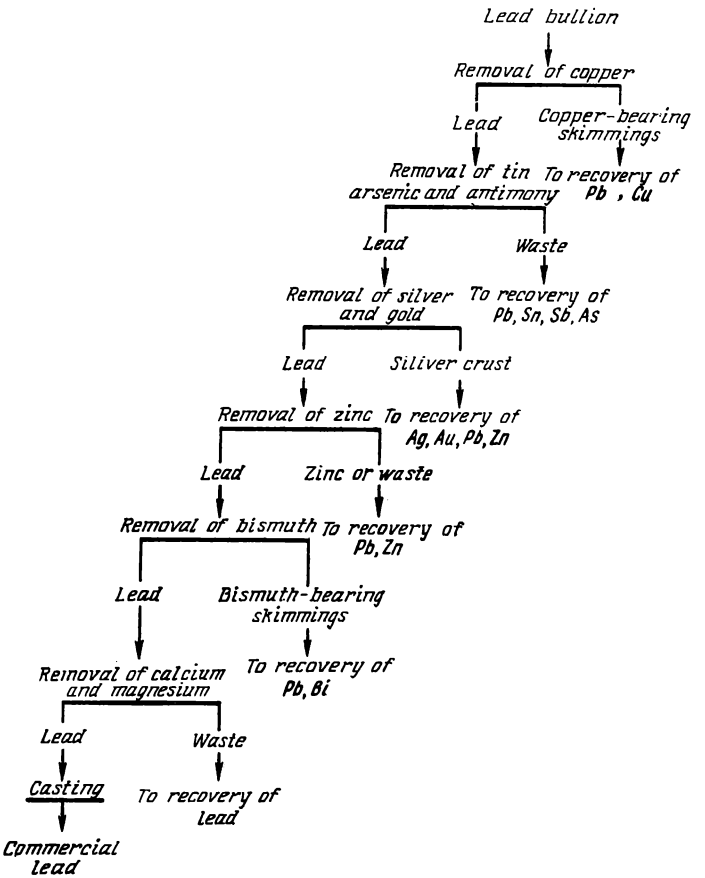


Fig. 60. Refining of lead bullion

and antimony are extracted from lead as waste suitable for subsequent winning of pure metals. A refining flowsheet is shown in Fig. 60.

The basic apparatus for operation according to the above flowsheet is a cast iron or steel kettle, heated by fuel oil, gas or electricity. Kettles are set in brickwork, as shown in Fig. 61. Combustion gases pass along a ring canal surrounding

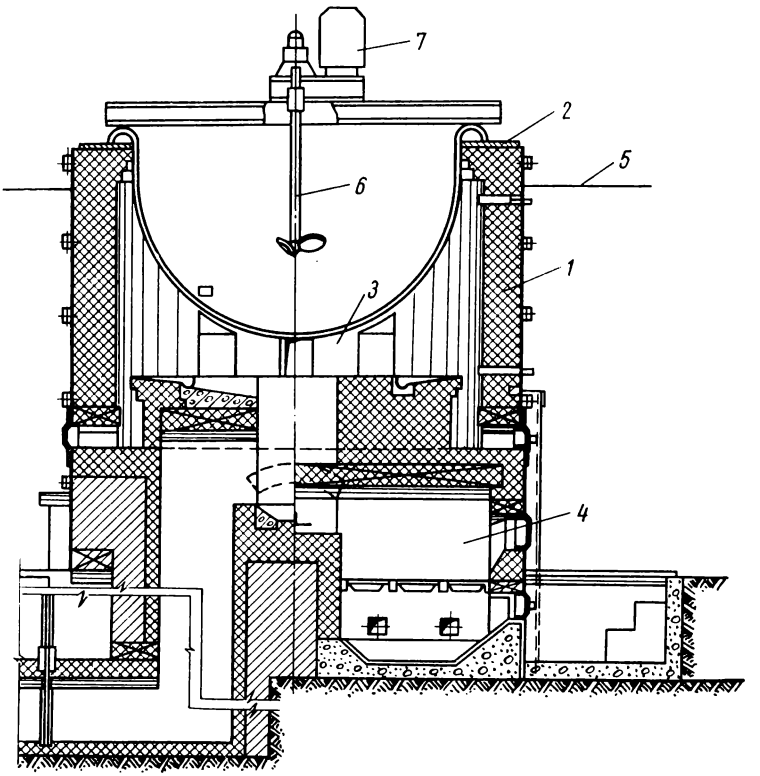


Fig. 61. Lead refining kettle
1—brickwork; *2*—mantle ring; *3*—bottom supports; *4*—firebox; *5*—working platform; *6*—stirrer; *7*—electric motor and gearbox

the kettle and are exhausted through a stack. Kettle capacity in terms of molten lead ranges from 150 to 350 tons. Kettles are filled and discharged by means of centrifugal pumps carried by an overhead crane from one kettle to another. Molten lead is agitated by portable stirrers (Fig. 61).

Rotating at a speed of 100 to 160 rpm, the stirrer makes the lead to stream downwards, forming a funnel at the surface of the molten metal. Reagents that are fed into this funnel are entrained by the stream of lead and distribute themselves uniformly throughout the volume of the kettle.

Automatic temperature control greatly simplifies lead refining and brings down operating costs. Of a great convenience in practice is electrical heating of the kettles.

Removal of Copper

Solubility of copper in lead decreases with the temperature. As lead cools, it gives off crystals of copper-lead solid solution having density of about 9 that float to the surface.

Copper removal is the better, the lower the temperature to which the melt is cooled. However, as temperature goes down, molten lead tends to become more viscous, this slowing down the floating of solid particles and causing skimmings to carry much molten lead.

In order to capture as less lead as possible, kettle is first cooled slowly to 450-500°C and dry "skimmings" are removed. Ladles with perforated bottoms, handled by overhead cranes, are used for the purpose. At 500°C, skimmings are powder-like and carry relatively little lead with them.

Lead is next poured into a similar kettle and cooled to 330-340°C, the skimmings then carrying a viscous mass permeated with molten lead. These "fat" skimmings are returned to the first refining stage.

The above operations are known as rough refining. It reduces copper content to 0.2-0.3% only. Elemental sulphur is mixed into molten lead at 330-350°C to ensure fine refining. Copper and sulphur give cuprous sulphide that floats as solid particles when the melt is allowed to settle. Fine refining skimmings are composed of Cu_2S and PbS. To minimize mechanical capture of lead, the temperature of the melt is raised to 370°C before skimming. After lead is treated with sulphur, its copper content is not more than 0.003%.

Sulphide skimmings, containing some 95% Pb and 3% Cu, are recycled together with "fat" skimmings to the first kettle when a fresh batch of lead is treated.

Treatment of dry copper-bearing skimmings is a separate complicated processing stage, requiring the recovery of copper and lead and the noble metals they carry in solution.

A more advantageous technique for primary refining of lead (copper removal) has been introduced of late at larger Soviet plants. Lead bullion is poured into an electric furnace or a gas-fired reverberatory furnace. Molten metal bath in the furnaces is up to 2 m deep and is heated to 800-900°C at the bottom, and to 450°C only at the top. A rich lead concentrate and soda (anhydrous) ash is fed to molten lead, the amount of the former being about 8%, and that of the latter, 1.5%. Copper is transformed to sulphide

$$2Cu + PbS \rightarrow Cu_2S + Pb \quad (143)$$

Soda forms sodium sulphide and sodium sulphate

$$4Na_2CO_3 + 4PbS \rightarrow 3Na_2S + 4Pb + 4CO_2 + Na_2SO_4 \quad (144)$$

Combined melting of sodium sulphide and sulphate results in a matte, which floats to the surface of the melt and whose melting point is in the neighbourhood of 650°C. It contains up to 15% Pb and 50% Cu, while refined lead runs not more than 0.4% copper. Subsequent fine refining by sulphur is carried out as described above.

Removal of Tin, Arsenic and Antimony

These impurities possess a greater affinity for oxygen than lead. To remove them, molten lead is treated with a molten NaOH and NaCl alloy which contains an oxidizer, saltpeter, to oxidize the impurities according to the reactions* below

$$2As + 2NaNO_3 + 4NaOH \rightarrow 2Na_3AsO_4 + 2H_2O + N_2 \quad (145)$$

$$2Sb + 2NaNO_3 + 4NaOH \rightarrow 2Na_3SbO_4 + 2H_2O + N_2 \quad (146)$$

$$5Sn + 4NaNO_3 + 6NaOH \rightarrow 5Na_2SnO_3 + 3H_2O + 2N_2 \quad (147)$$

A small amount of lead is concurrently oxidized to sodium plumbite

$$5Pb + 2NaNO_3 + 8NaOH \rightarrow 5Na_2PbO_2 + N_2 + 4H_2O$$

* Similar reactions of this type are also possible in reduction of the saltpeter nitrogen to ammonia, but they are of a much lesser importance.

Sodium chloride does not participate in the process, but is intended to increase the volume of the salt melt and to reduce the latter's viscosity.

Given below is the consumption of reagents (in kg) per kilogram of impurity being removed:

	NaOH	$NaNO_3$	NaCl
As	2.9	1.0	1.0
Sn	1.8	0.6	0.6
Sb	1.5	0.6	0.5

Apparatus for this processing stage (Fig. 62) is fitted with a pump for transferring lead from the kettle to the working (reaction) cylindrical tank upon a layer of molten salts. The jet of lead is broken to small droplets of a greater aggregate surface area which is essential for a rapid oxidation of impurities. After passing as droplets through the layer of molten salts, the lead flows to the kettle where it is again sucked by the pump and recirculated through the reaction tank until the specified purification is attained.

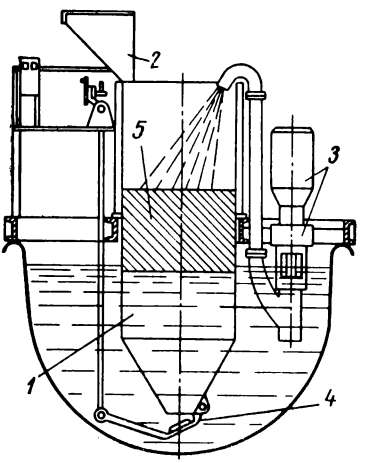


Fig. 62. Apparatus for alkali refining of lead

1—reaction tank; *2*—saltpeter hopper; *3*—pump and motor; *4*—valve; *5*—layer of salt melt

Salts formed by impurities remain in the melt as suspensions. As they accumulate in the alkali alloy, the latter thickens, this being a symptom indicating the necessity for alloy replacement. The valve is then closed, and as lead accumulates in the tank, it displaces the alloy into a prepared ladle, the apparatus finally being supplied with a fresh portion of the alkali alloy.

Impurity-saturated alloy is processed by a hydrometallurgical technique to calcium arsenate, used in agriculture, to sodium antimonate, utilized in smelting of antimony, and to alkali which is re-employed for lead refining. Tin is

usually low in lead, and it accumulates but rarely in the molten mixtures. None the less, a number of techniques have been developed for recovering tin compounds.

Removal ol Silver and Gold

Silver and gold are removed in a process known as desilverization by introducing zinc into molten lead at a temperature of about 450°C, the zinc combining with silver and gold to give chemical compounds whose melting points are as follows, °C:

Ag_2Zn_3 . .	665	Au_2Zn_5 . .	664
Ag_2Zn_5 . .	636	$AuZn_5$ . . .	475
AuZn . . .	725		

Besides, zinc interacts with silver and gold to give numerous solid solutions whose melting points are higher than that of lead. Chemical compounds and solid solutions of zinc and noble metals are of a lesser density, and they float and form on the surface of molten lead a crust of silvery or zincky froth.

Zinc is partly soluble in lead, its excess also floats above lead as saturated solution of lead in zinc. Thus, the crust on the surface of lead is a complex product containing noble metals, lead and zinc. The contaminating arsenic, antimony and tin increase the consumption of zinc, interfere with the separation of crust, and, therefore, they should be removed first.

Noble metals are removed from lead in the same steel kettles. Zinc is introduced in several steps by means of a stirrer. A few crusts are skimmed in succession. The initial ones are rich and the latter, low in noble metals. Crusts low in noble metals are recycled.

A first addition at 500°C is a lean crust from a preceding treatment. Once kettle contents are completely melted, they are stirred for 20-30 min, then cooled to 450-480°C. Then the first crust is skimmed. The procedure is repeated after subsequent additions are introduced.

The second and subsequent additions of zinc are introduced in accordance with silver and gold contents in the metal. Before each addition, lead is heated to 450-480°C,

and before crust is skimmed, cooled to 340-350°C. Three zinc additions are generally sufficient to bring down silver content to 3 g/t.

The whole treatment cycle, heating and cooling of lead included takes 10 to 12 hours. Zinc consumption depends on the composition of lead being treated and amounts generally to 1-1.5% (by mass), whereas fuel consumption is about 3% of the mass of lead.

Rich crust, after part of lead is melted out (liquated) or squeezed under a press, has the following composition: 10% Ag, 25% Zn and 65% Pb.

Treatment of Zinc Crust

Zinc is removed from crust by distillation, advantage being taken of the zinc's greater volatility as compared to lead and noble metals. In a now obsolete practice, distillation was carried out in graphite retorts and coke furnaces over a period of 5 to 8 hours at a temperature between 1100 and 1200°C. Oxidation of zinc was avoided by charging 3-4% by crust mass of charcoal or fine anthracite into the retort together with the crust. However, part of zinc resists distillation and remains in the retort as semi-oxidized dust or dross.

The present-day practice is to treat crust for zinc removal in round three-electrode electric furnaces in ratings of up to 0.5 MW (Fig. 63). Graphite electrodes are dipped into a slag of sodium and calcium silicates that covers molten crust.

Crust is charged by a mechanical feeder, coke fines being added in amounts of 2 to 3%. Some 90% of zinc are driven off at a temperature of about 1250°C, and most of it is collected as molten metal in a condenser fitted with a stirrer, the balance being settled out in a dust collector. Distillation residue, silvery lead with not more than 2% Zn, is discharged via a siphon. Molten zinc from condenser is cast into pigs and recycled for the removal of noble metals.

Silvery lead, whatever its origin, is treated by cupellation which essentially is oxidation of lead to PbO in small reverberatory furnaces at 1200°C by vigorous interaction with air blast.

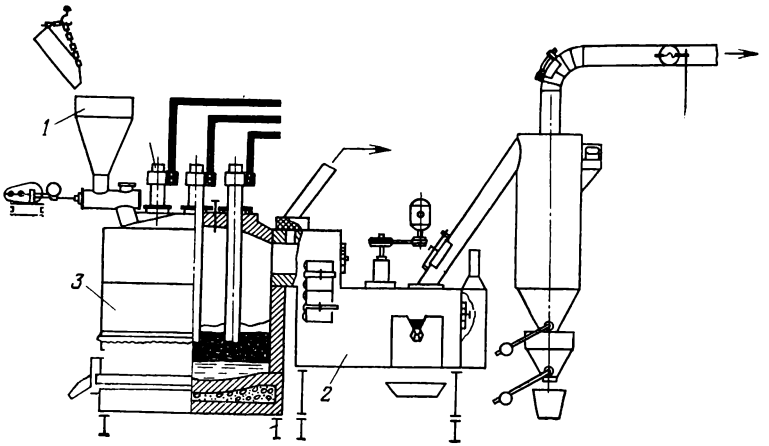


Fig. 63. Round three-electrode furnace for distillation of zinc from crust

1—feeder; *2*—condenser; *3*—electric furnace

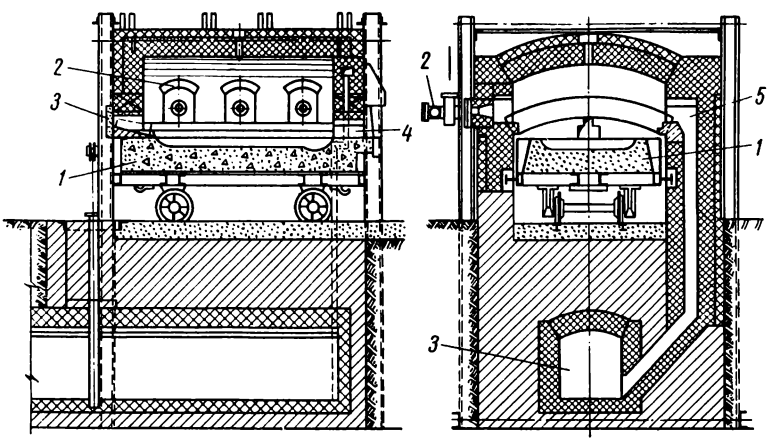


Fig. 64. Cupellation furnace

1—draw-out cupel; *2*—burners; *3*—air supply device; *4*—litharge discharge hole; *5*—flue

The bath of the cupellation furnace, cupel, is built of magnesite brick enclosed in a steel casing and set on a car, walls being protected by water jackets (Fig. 64). Molten litharge (lead oxide) that floats to the surface of the alloy is gradually withdrawn, and the bath is charged with fresh portions of silvery lead so as to accumulate gold and silver.

After the bath has been filled with the alloy containing accumulated gold and silver, the remaining lead is completely oxidized. Small amounts of litharge formed in this operation are soaked by the cupel walls. The gold and silver alloy is poured into molds and shipped to affinage plants for refining and separation to obtian gold and silver.

Removal of Zinc

Once desilverized, lead carries an excess of zinc in amounts equal to about 0.7% of the mass of the metal.

There is a number of techniques for removing zinc, frequently used today is vacuum sublimation. An apparatus for implementing the technique (Fig. 65) is handled by a crane and set on a standard kettle. A steel cylindrical bowl with a water-cooled bottom is fitted on the apparatus frame with the bottom up. The bowl communicates with a vacuum pump. A steel tube passes in the axis of the bowl and houses the lead pump shaft. Pipes with impellers and steel disks at their ends branch off the pump upwards. The lead pump is started at 600°C and a residual pressure of about 6.66 N/m^2 (0.05 mm Hg). Lead is continuously supplied to side pipes and splashed in the vacuumized space, while falling droplets are additionally broken on the steel disks. A large aggregate surface area of droplets promotes rapid volatilization of zinc.

Zinc vapours condense together with some lead as large crystals on the bowl bottom. After a 5-hour operation of the apparatus lead carries a mere 0.3-0.5% Zn. The apparatus is taken off the kettle, and the condensate with 60% Zn and 40% Pb is hacked off the bottom. This condensate is suitable for lead desilverization.

At many a plant, zinc is also removed by an alkali technique similarly to tin, arsenic and antimony which differs in that no saltpeter is required. Zinc is readily oxidized by

alkali according to the reaction

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2 \qquad (148)$$

Spent alloys are leached by water to recover zinc oxide and to regenerate the alkali.

Vacuum refining is superior to the alkali technique in that it allows a part of the zinc to be separated as a lead

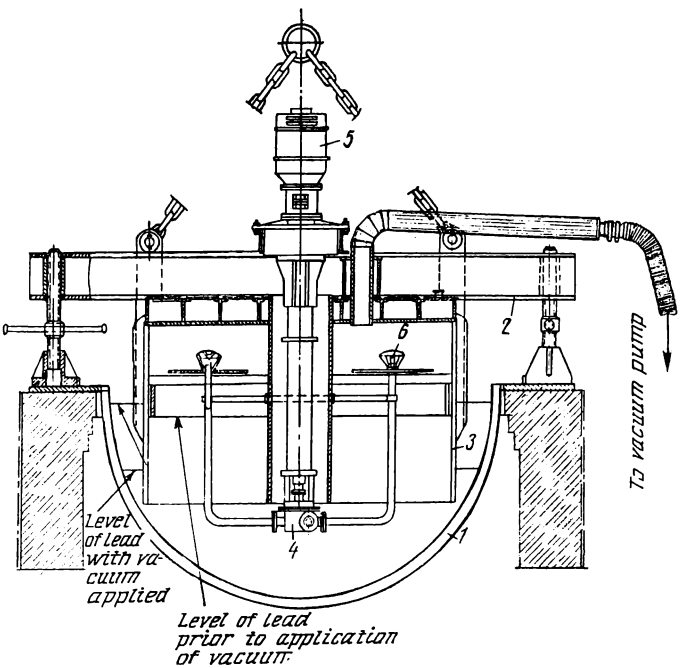


Fig. 65. Apparatus for vacuum sublimation
1—kettle; *2*—frame; *3*—steel shell with cooled bottom; *4*—pump; *5*—pump motor; *6*—side pipes with pulverizers and deflecting disks

alloy which is suitable for the recovery of noble metals. However, vacuum refining fails to yield commercial lead, and requires the removal of residual zinc by an alkali method (148).

Removal of Bismuth

Bismuth may be removed at a temperature of about 350°C by adding to lead some magnesium and calcium which combine with bismuth to give chemical compounds and solid solutions that are insoluble in metallic lead and float to its surface. Melting points of some of the compounds are given below, °C:

Bi_3Ca	507
Bi_2Ca_3	928
Bi_2Mg_3	715

When calcium only is used, bismuth content can be brought down to 0.05% and when calcium and magnesium are used together, down to 0.008%. Subsequent small addition of antimony reduces bismuth content to 0.004-0.006% because of the formation of intermetallic compounds of the type $Ca_xBi_mSb_n$ that are insoluble in lead.

Magnesium is introduced into lead as pigs, and calcium, as a 3% alloy with lead. Lead-calcium alloy is prepared on the spot. Most of calcium tends to oxidize if melted directly with lead, and, therefore, lead is first alloyed with sodium, then treated by molten calcium chloride at a temperature of about 700°C:

$$\{Pb-Na\}_{alloy} + CaCl_2 \rightleftarrows \{Pb-Ca\}_{alloy} + 2NaCl$$

The additions are introduced in 2 steps: 3/4 of the calculated amount are introduced first, then the balance. After a 30-min stirring rich bismuth skimmings are removed and treated for recovery of bismuth. Skimmings from the second portion of additions are recycled. Next, ground antimony is mixed in after the surface of lead is thoroughly skimmed.

Bismuth skimmings are remelted and cast into anodes for electrolysis, where bismuth goes into anode mud, from which it is finally melted out.

Removal of Magnesium and Calcium

After removal of bismuth lead still runs some magnesium, calcium and antimony, and, sometimes, zinc from vacuum refining. All these impurities are removed simultaneously by an alkali technique through oxidation by a small

addition of saltpeter or without it. After this final purification, lead is cast into moulds.

The multi-stage pyrometallurgical lead refining technique described in the present paragraph is complicated and labour-consuming. Up to 25% of lead goes to waste, direct recovery to commercial metal but rarely exceeding 75%. Despite this fact, pyrometallurgical refining is a chief purification technique in modern metallurgy of lead.

Electrolytic Refining

On the face of it, electrolytic refining would seem to be a more advantageous technique as it allows manufacture of a pure metal in one processing step only, electrolysis, with a recovery of 96 to 98% Pb. However, all impurities are collected in a single product, slime of a rather complicated composition, whose complex processing is as yet a problem. Extensive use of electrolysis is also prevented by the unavailability of a perfectly suitable electrolyte, since the solutions at hand are either too costly or toxic.

Silicofluoride electrolyte, which contains 18% $PbSiF_6$ and 8% H_2SiF_6, allows a successful refining of lead subsequent upon a rough drossing. The process yields lead of grade CO against a current efficiency of 97-98%. Copper forms a solid insoluble crust on the surface of anodes. Regretfully, the preparation of this electrolyte necessitates a toxic and very corrosive fluoric acid. Vapours given off by the electrolyte in electrolysis are toxic as well. At some plants, silicofluoride solutions are used for the electrolysis of remelted bismuth skimmings. Bismuth passes to slime where its content goes up to 60-70%. Slime is processed to yield bismuth.

The electrolyte, which carries sulfamic acid HNH_2SO_3, also requires a preliminary rough separation of lead. It is non toxic, allows to remove all impurities from lead and obtain metal grade CO.

Electrolysis is conducted in reinforced concrete tanks protected on the inside with asphaltum or vinyl plastic. Each tank houses up to 20 190-kg anodes. Cathodes are manufactured from sheets of pure lead about 1 mm thick.

Electrolyte composition is, g/lit: 130 Pb, 5 sulfamic acid, 6 phenol, 3 gelatin, 5 colligneol. Cathodic current density is 120 A/m^2; voltage across tank, 0.5 V; current efficiency, 96%; power consumption, about 100 kWh/t.

Anode mud contains: 15% Pb; 5% Ag; 10% Cu; 30% Sb; 10% As. In smelting of anode mud to metal, 80% Ag only are recovered, the balance distributing itself between slag and dust. Distribution of bismuth between smelting products is even less satisfactory.

34. Refining of Gold and Silver

Manufacture of Gold and Silver from Alloys

Noble metals are separately manufactured from alloys, and impurities they contain, at adequately equipped refining plants. Gold industry plants ship their doré ingots (French, d'ore, gold) from remelting of copper electrolysis anode mud and silvery crust processing to gold-refining plants. In Soviet practice, the content of noble metals in alloys is customarily described by purity standards, or thousandths of mass.

Typical compositions of incoming raw materials are given below, in purity standard values:

	Au	Ag	Pt	Pd
Doré metal from copper electrolysis anode mud	60	900	1	2
Doré metal from lead refining	20	970	—	0.05
Scrap and coins	0.5	700	—	—

Separate batches of these materials are not homogeneous, and, therefore, to ensure an equitable settling of accounts with suppliers, the assays are averaged by making an acceptance heat in induction furnace and testing resultant ingots.

Starting alloys are contaminated by zinc, lead, copper, iron, sulphur, tellurium and other elements which when taken as an aggregate are termed *master alloys.*

To separate the bulk of silver and the master alloy, melts are blown with chlorine for 1 to 3 hours at a temperature of about 1150°C. A mixture of borax and quartz is charged on melt surface to give a primary slag which is subsequently supplemented by the floating chlorides.

All elements, except for gold, are chlorinated and partly sublimated, but their bulk goes into slag. Data below on isobaric potentials of formation of chlorides at 1200°C and their melting points may serve as a rough guide on the order of chlorination of elements involved:

Chloride	$AuCl_3$	$PtCl_2$	$PdCl_2$	$FeCl_3$	AgCl	CuCl	$PbCl_2$	$ZnCl_2$
ΔZ	>0	5	12	45	60	75	100	140
Melting point, °C	—	—	—	315	1550	1366	950	732

The above treatment yields gold of purity standard 995 which is stored as gold bullion or additionally purified by electrolysis as indicated below. The latter is always necessary when content of platinum group metals is high.

Chloride slag is composed chiefly of AgCl and CuCl. It is crushed, charged into bags, then placed in a tank with diluted sulphuric acid together with sheets of iron. Silver is then reduced by ions Fe^{2+}

$$AgCl + Fe^{2+} \rightarrow Ag + Fe^{3+} \qquad (149)$$

$$K = \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}; \quad pK = \frac{0.77 - 0.80}{0.06} = -0.5$$

copper chloride oxidizes

$$CuCl + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+} + Cl^- \qquad (150)$$

As ions Cu^{2+} pass through bag cloth, they are displaced by iron (34). Ions Fe^{3+} are also reduced by iron, and, therefore, their content in the solution is low, equilibrium of reaction (149) being shifted to the right. A sufficiently complete reduction of silver is attained in two days at a temperature of the solution of 90-100°C.

Substituted silver deposit is pressed, melted and cast into 10-kg anodes as slabs about 10 mm thick, whose gold assay should not exceed purity standard 200, and master alloy assay, purity standard 75.

Electrolysis of Silver

The electrolyte is a solution of $AgNO_3$ with about 100 g/lit of Ag. Potentials of solution of silver at the anode and of its reduction at the cathode are close to values given in Table 3, which also shows that copper dissolves in advance of silver and accumulates in the electrolyte. Equation (26) tends to indicate that copper cannot contaminate the cathode deposit. None the less, contamination takes place because of concentration polarization. Therefore, current density should not exceed 400-600 A/m^2, the electrolyte should be stirred vigorously and accumulation in it of more than 100 g/lit Cu^{2+} should be prevented.

Presence in the alloy of gold in purity standard of more than 200 Au passivates the anodes with the effect that oxygen evolves according to reaction (24), voltage across tank increasing accordingly.

Solution of platinum and palladium is possible in the presence of even the smallest amount of gold because of concentration polarization

$$Pd - 2\bar{e} \rightleftarrows Pd^{2+}; \quad E^\circ = 0.99 \text{ V} \qquad (151)$$

$$Pt - 2\bar{e} \rightleftarrows Pt^{2+}; \quad E^\circ \simeq 1.2 \text{ V} \qquad (152)$$

Understandably, ions of the above metals may be reduced at the cathode in advance of silver and so contaminate it. Therefore, their accumulation in the electrolyte should not exceed, g/lit, 0.025 and 0.2 respectively.

Cathodic current efficiency with respect to silver is 95%. It goes down when a simultaneous discharge of NO_3^- takes place, possibly according to reactions

$$NO_3^- + 2H^+ + \bar{e} \rightleftarrows NO_2 + H_2O; \quad E^\circ = 0.80 \text{ V} \qquad (153)$$

$$NO_3^- + 4H^+ + 3\bar{e} \rightleftarrows NO + 2H_2O; \quad E^\circ = 0.96 \text{ V} \qquad (154)$$

$$NO_3^- + 10H^+ + 8\bar{e} \rightleftarrows NH_4^+ + 3H_2O; \quad E^\circ = 0.87 \text{ V} \qquad (155)$$

Nitrogen oxides evolve (153, 154)*, probably, at an overvoltage, which comes down if the electrolyte carries more

* Similar reactions with the formation of NO_2^- and N_2O_{gas} are a possibility, but they are not considered here.

than 20 mg/lit Te, this explaining why the latter is removed to a greatest possible extent by thorough washing of cement silver, obtained from chloride.

Cathodic starting sheets are made of thin sheets of silver or aluminium. The deposit does not make a strong bond with them. Large loosely interconnected crystals fall to the tank bottom, from where they are removed by skimmers.

When anodes dissolve, gold separates as mud which contains also some Ag_2Se, platinum, platinum group metals and other compounds. Cathodes are coated with a vinyl chloride cloth to prevent contamination of cathodic silver by mud.

Tanks having capacities of up to 0.6 m^3 are built of vinyl plastics and reinforced with wooden or iron frameworks. Temperature of the electrolyte is maintained at about 40°C at the expense of heat given off by the passing current. The solution is air agitated. Voltage across tank ranges from 0.8 to 2.6 V, depending on electrolyte composition and current density, and the power consumption is 300-600 kWh/t.

Silver deposit, after it is washed with diluted nitric acid and water and remelted, has a purity standard 999.9. On special order, customers may be supplied with silver of a purity standard 999.99 or 999.999 which is obtained by a second electrolysis.

Spent electrolyte is stripped of silver in separate tanks with anode from low-standard alloys, while remaining Ag^+ is then settled out as chloride.

Electrolysis of Gold

Treated by electrolysis is a metal from chlorination and mud from electrolysis of silver, after they have been treated by a multi-stage chemical refining. All this is melted in induction furnaces and cast into rectangular anodes of a mass of 2 or 3 kg.

The latter are contaminated by silver, platinum group metals and relatively small amounts of master alloy.

The electrolyte is a solution of $HAuCl_4$ and HCl (up to 200 g/lit Au and 80 g/lit HCl). Gold dissolves according

to reactions

$$Au + 4Cl^- - 3\bar{e} \rightleftarrows AuCl_4^-; \quad E^\circ = 0.93 \qquad (156)$$

$$Au + 2Cl^- - \bar{e} \rightleftarrows AuCl_2^-; \quad E^\circ = 1.11 \qquad (157)$$

The latter reaction (157) is possible because of a concentration polarization due to either a high current density of formation of a crust of AgCl at the anode.

Anions $AuCl_2^-$ disproportionate to give a metallic deposit that settles out as mud

$$3AuCl_2^- \rightleftarrows AuCl_4^- + Au + 2Cl^- \qquad (158)$$

Concentration of trivalent Au in the electrolyte greatly exceeds that of divalent Au.

In case of a low acidity and temperature, gold anodes passivate, their solution ceases and chlorine evolves according to reaction (29), while oxygen fails to evolve through reaction (24) apparently because of its high overvoltage on gold. Electrolysis is conducted at a temperature of 50-60°C and a HCl content of about 60 g/lit.

Platinum and palladium dissolve at the anode according to reactions

$$Pt + 4Cl^- - 2\bar{e} \rightleftarrows PtCl_4^{2-}; \quad E^\circ = 0.73 \text{ V} \qquad (159)$$

$$Pd + 4Cl^- - 2\bar{e} \rightleftarrows PdCl_4^{2-}; \quad E^\circ = 0.62 \text{ V} \qquad (160)$$

Master alloy constituents—copper, lead, bismuth, iron, tin, antimony and other metals form simple ions or complex chlorides, and they generally have no effect upon the solution of anodes.

Iron that goes in solution as Fe^{2+} reduces gold, increasing the latter's transfer to mud

$$AuCl_4^- + 3Fe^{2+} \rightarrow Au + 3Fe^{3+} + 4Cl^- \qquad (161)$$

Silver gives an insoluble chloride according to reaction

$$Ag + Cl^- - \bar{e} \rightleftarrows AgCl; \quad E^\circ = 0.22V \qquad (162)$$

If the alloy carries less than 5% Ag, AgCl settles in the mud, but if silver is present in greater quantities, AgCl coats the anode with a strong crust and prevents its solution.

Gold anodes with up to 20% silver can be dissolved by a Wohlwill technique which involves asymmetric current.

To this end, an alternating current approximating in intensity the electrolysis direct current is caused to flow through the tank together with the direct current.

It is readily apparent from Table 3 that the probability of the cathodic deposit being contaminated by impurities is quite low. However, platinum and palladium may settle together with gold, particularly at a high current intensity. To avoid this, concentration of platinum is kept below 50 g/lit, and that of palladium, below 15 g/lit. The concentration of other impurities in the solution should be maintained below, g/lit: Cu, 90; Pb, 1.5; Fe, 2; Te, 4.

Spent electrolyte is stripped of gold in separate electrolysis tanks with graphite anodes, and then it is treated by various other techniques to recover the remaining gold and platinum group metals.

Electrolysis of gold is carried out in porcelain, less frequently, in vinyl plastic tanks of 25-litre capacity. Anodes, 15 of them, are suspended on silver bars, three in a row, a cathode of corrugated gold foil 0.2 mm thick being placed opposite each row. The tanks are placed inside water baths, the electrolyte is agitated by bubbling air.

Aggregate density of direct and alternating currents attains 1500 A/m^2, and voltage across tanks is about 1 V. The purity of the cathodic deposit after mechanical cleaning by brushes and subsequent washing in nitric acid and ammonia is purity standard 999.9.

Review Questions

1. What is the usual valency of lead in metallurgical processing products?

2, 3, 4.

2. What valuable metals, in addition to lead, do polymetallic ores carry?

Zn, Mo, Cu, Pt, Ag, Au, Cd, Bi, Al, Se, Te.

3. What methods are used for dressing polymetallic ores?

Gravity concentration, magnetic separation, bulk flotation, selective flotation, electrostatic dressing.

4. What types of furnaces are used to smelt lead bullion?

Reverberatory, blast, electric furnaces.

5. What is the succession of removal of impurities from lead in refining?

Au, Ag, Zn, Bi, Cu, As, Sb.

CHAPTER 5

METALLURGY OF ZINC

35. Chemical Properties of Zinc

Zinc is in group II of the periodic table of elements. It is divalent and possesses clear-cut metallic properties. As a metal, it is inferior in activity to beryllium, magnesium and alkali-earth metals which make up the chief subgroup of the same group.

Ordinal number of zinc is 30, and it is the last one in the series of transitional metals.

Zinc has been known from ancient times as an alloy with copper. There are data on its use in India and China in the 5th century, but commercial manufacture of zinc began in England in the 18th century only.

Melting and boiling points of zinc are 427 and 907°C respectively. A relatively low boiling point has somewhat hampered the development of zinc manufacture. Customary techniques for smelting metals by heating a mixture of ore and coal proved to be ineffective because of the volatility of zinc which escaped with the flue gases as vapour. At a later date methods were evolved to condense these vapours, and this has given rise to the distillation zinc manufacture.

Naturally occurring zinc of an atomic mass of 65.37 consists of five isotopes Zn^{64}, Zn^{66}, Zn^{67}, Zn^{68}, Zn^{70}.

A large negative value of the chemical potential is characteristic of the high activity of zinc. However, it fails to decompose cold water not only because it is coated by a thin film of basic carbonates, but due to a slow discharge of hydrogen ions on zinc caused by a high hydrogen overvoltage (Table 6).

Iron, copper and other electropositive metals greatly speed up solution of zinc in acids.

To protect iron against corrosion, it is plated with a coat of zinc. Should the coat be damaged at any point, its pro-

tective properties remain unaffected, since base sections of iron are not attacked, but are points where hydrogen evolves from a solution of zinc.

In strong acids, such as HCl and H_2SO_4, zinc dissolves with an evolution of hydrogen, and in alkali liquors, and in molten alcali with the formation of zinc acid anions, or zincates (148).

Zinc oxide ZnO, a fine crystalline white powder obtained by oxidation of zinc vapours in the air, finds extensive use in the manufacture of oil and other types of paints owing to its white colour and high covering power.

Zinc oxide is a non-fusible substance which volatilizes at a temperature above 1800°C without melting. Reduction of zinc from its oxide by carbon begins at a temperature of about 950°C.

Zinc sulphide ZnS is also non-fusible and appreciably volatile at a temperature in excess of 1180°C. When heated in the air, ZnS oxidizes to basic sulphates $ZnO \cdot nZnSO_4$, sulphate $ZnSO_4$ and oxide ZnO.

36. Raw Materials for Manufacture of Zinc

Zinc-bearing minerals from which metallic zinc can be manufactured are very few and were discussed in par. 29.

Zinc ores contain 2.0-12% Zn and some copper, lead and a number of other valuable metals. Polymetallic lead-zinc ores were described above, and we shall limit ourselves to information concerning zinc concentrates obtained by selective flotation of polymetallic ores.

Zinc concentrates carry, %: 47-60 Zn, 1.5-2.5 Pb, up to 3.5 Cu, 3-10 Fe, up to 0.25 Cd, 29-33 S, and small amounts of thallium, indium, gallium, germanium, selenium and tellurium. A mineralogical composition of a zinc concentrate (47.66% Zn) may be described by the percentages below:

Sphalerite	70.3
Galenite	5.2
Chalcopyrite	3.1
Pyrite and other iron sulphides	11.3
Silicates and carbonates	10.1

Flotation zinc concentrates are powders composed of 50 to 95% of particles finer than 0.07 mm and not more than 0.1 to 0.3% of particles larger than 0.6 mm.

Dressing of oxidized ores yields concentrates in which zinc is chiefly in the form of smithsonite and calamine, $Zn_2SiO_4 \cdot H_2O$.

37. Zinc Manufacturing Techniques

Today zinc is obtained by a pyrometallurgical (distillation) and a hydrometallurgical (electrolytic) techniques. The former was introduced industrially much earlier than the latter. Abroad, about half of zinc output is produced by distillation.

Soviet zinc metallurgy developed chiefly by way of electrolysis.

Distillation Technique

Distillation in horizontal retorts. Zinc concentrate is roasted to transform sulphides into oxides, sphalerite oxidizing according to reaction (134). A mixture of roasted zinc concentrate with anthracite fines or coke crush is charged into fireclay retorts (Fig. 66) that are set horizontally in a furnace heated to 1400°C.

In a retort, zinc is reduced by the reaction

$$ZnO + CO \rightleftarrows Zn_{vapour} + CO_2 \qquad (163)$$

$$K_p = \frac{P_{Zn} \cdot P_{CO_2}}{P_{CO}}$$

The equilibrium constant of the reaction includes partial zinc vapour pressure which is not in equilibrium with molten metal since the latter is lacking. The mouth of the retort opens into a condenser from refractory clay. Molten zinc is scooped out of the condenser as it accumulates. However, not all of zinc vapours have time to condense, and part of them passes into a steel allonge (a receiver) that is put on the condenser outlet, where the temperature is below the melting point of zinc and fine metallic droplets oxidize from the surface with the effect that zinc settles as a fine powder, termed blue powder.

The retort may be the site of reduction of other metals the charge carries, e.g., cadmium, lead, copper. However, cadmium and lead only tend to volatilize in any appreciable amounts and are liable to contaminate zinc. The dependence

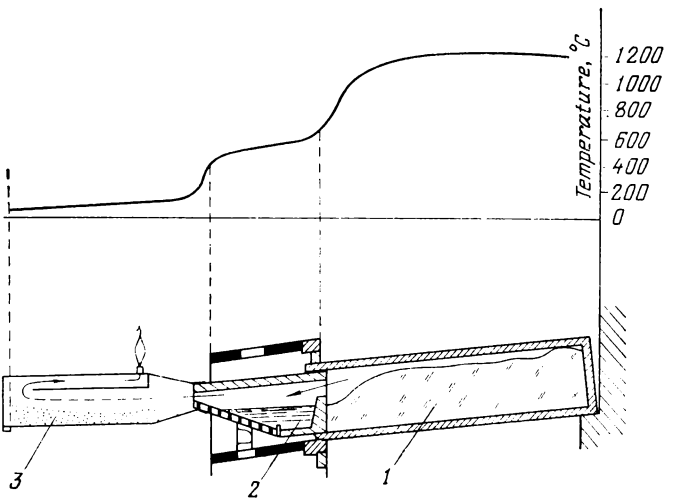


Fig. 66. Reduction of zinc in horizontal retort
1—retort; *2*—condenser; *3*—allonge (zinc vapour receiver)

of zinc vapour pressure on temperature is shown in Fig. 67. During distillation, molten zinc is repeatedly scooped because of a small condenser capacity, and once the process is over the condenser is removed, while the sintered distillation residue, zinc retort slag, is discharged from the retort. Zinc retort slag contains from 6 to 12% Zn. Recovery of this zinc requires a different treatment of the zinc retort slag.

Pyrometallurgical technique for obtaining zinc in horizontal retorts is essentially very simple, but of a low productivity, and resultant zinc is contaminated bylead and cadmium.

A horizontal retort should measure 300-370 mm across at the most, and its wall thickness should be limited to 30 to 50 mm. Should these dimensions be exceeded, transfer of heat inside the charge and, hence, the distillation rate are

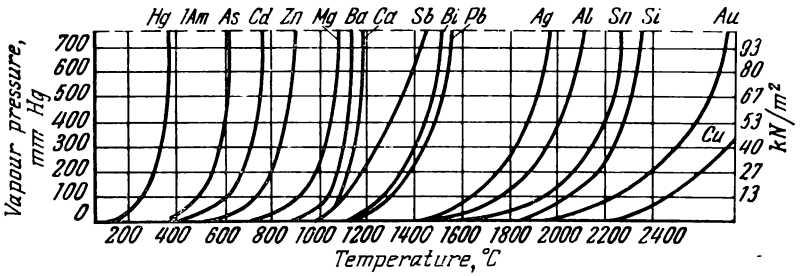


Fig. 67. Metal vapour pressure versus temperature

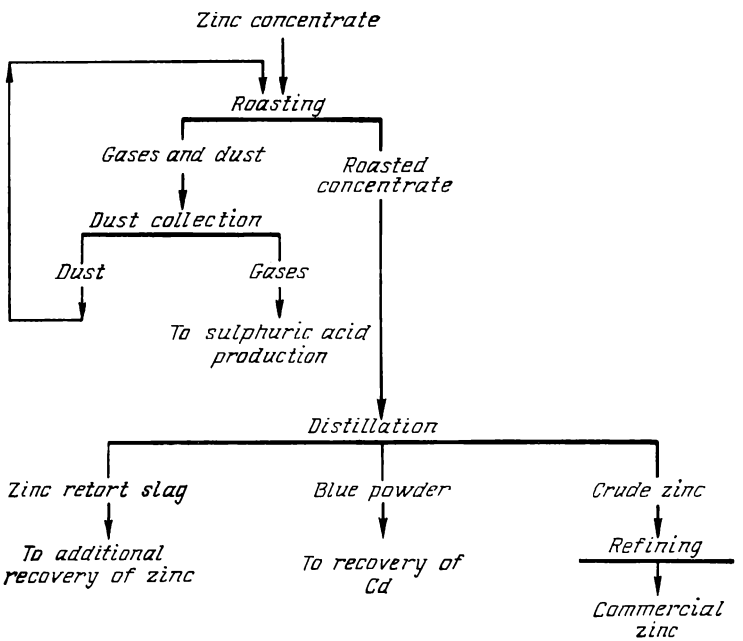


Fig. 68. Flowsheet for distillation manufacture of zinc

materially lowered. Length of a retort should be kept within 1700 to 1900 mm, otherwise it will fail under bending stresses at 1400°C.

A retort of above size has capacity for 80-90 kg of charge that contains some 30 kg of zinc. With a distillation cycle time of 24 hours and a yield of molten zinc of 80-83%, a single retort's productive capacity is not more than 25 kg of zinc per 24 hours. Therefore, a modern zinc smelter of medium capacity requires the operation of several thousand retorts. Even today, retorts are serviced manually, since all attempts to mechanize their handling, an arduous physical labour, have failed.

A general flowsheet for zinc manufacture is given in Fig. 68. The flowsheet has suffered practically no modifications as compared to the technique that was introduced initially, although distillation underwent considerable improvements and is now practised in a number of variants.

Distillation in vertical retorts. It became possible to make larger retorts and mechanize their handling only after the retorts have been placed vertically and manufactured from carborundum.

Carborundum is a silicon carbide of chemical formula SiC and melting point above 2700°C. Carborundum refractory items are manufactured by mixing carborundum powder with 6 to 12% (by mass) of refractory clay. The mixture is moistened and moulded, then dried and burned at 1400-1600°C. Resultant refractory items are rated to retain mechanical strength at temperatures up to 2000°C, are chemically neutral and 3-4 times more heat conductive than fireclay ones.

A vertical retort is a shaft of rectangular cross-section assembled of carborundum slabs or laid of carborundum brick, as shown in Fig. 69.

Generator gas, used to heat the retort, is burned in chambers that flank the retort on both sides. The height of the heated zone is about 7.5 m, and inside dimensions of retort cross-section average 300 × 1500 mm. The charge is introduced from the top as briquettes, while zinc retort slag, still retaining briquette shape, is discharged continuously at the bottom. The retort is fitted at the top with a refractory brick chamber for feeding the charge and removing zinc

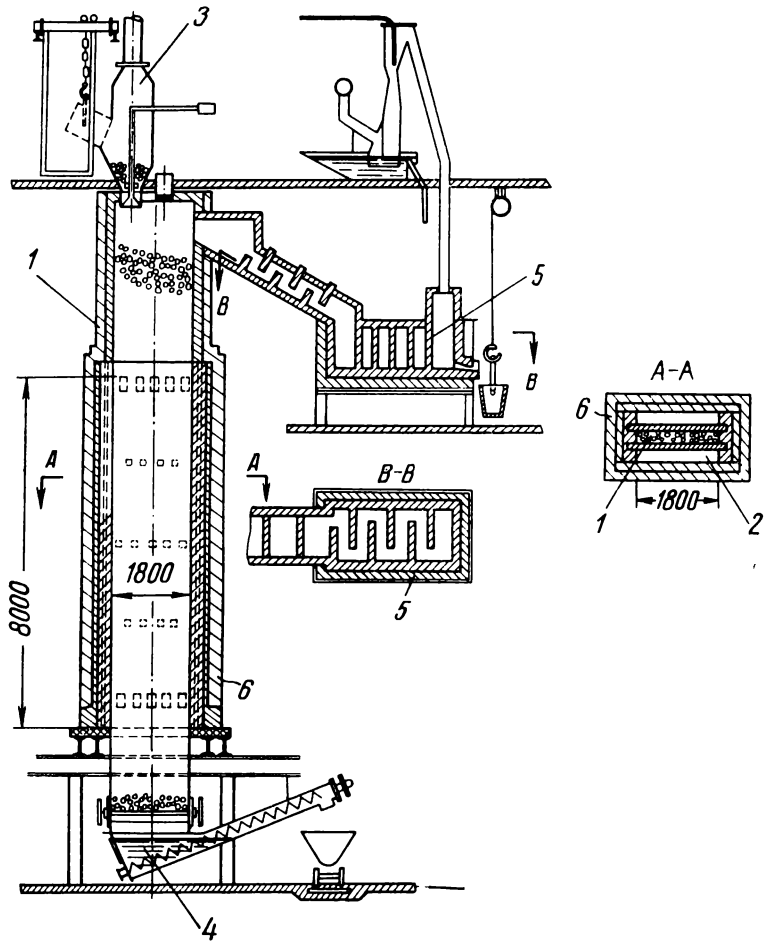


Fig. 69. Vertical retort for continuous distillation of zinc

1—carborundum retort; *2*—gas combustion chamber; *3*—charging device; *4*—water seal for discharge of zinc retort slag; *5*—condenser; *6*—refractory brick walls

vapours. The bottom of the retort ends in an iron box equipped with a water seal.

The charge if compounded of roasted zinc concentrate, anthracite, coking coal and a binder (e.g., coal tar or sulphite-pulp lye). After a thorough mixing, the charge is passed through a briquetting press. Next, briquettes are heated to 750-900°C, coal and tar are coked in the process to strengthen briquettes and making them adequately porous.

Distillation in vertical retorts is no different in chemistry than the standard horizontal retort technique. Heat conductivity of carborundum walls and briquetted charge is higher than that in standard distillation, and, therefore, zinc is removed more completely, its content in zinc retort slag being generally less than 5 or even 3%.

A condenser is lined with refractory brick and provided with internal partitions that lengthen the path of gases.

Condenser gases are directed to a scrubber where remaining zinc is collected as a fine dust. Cleaned gases are burned inside the retort, this effecting a saving of up to 20% of fuel.

A scrubber is a high tower provided with an internal packing of piled wooden planks, ceramic rings or other materials. The packing is sprayed with water at the top, and dust-laden gas is admitted from below. As it comes into contact with a film of water that trickles down, dust is wetted and entrained by water as pulp (Fig. 70).

Service life of a vertical retort is 3 to 5 years, and capacity, about 7 tons of zinc per 24 hours, or up to 90 kg per square metre of heat-conductive wall in 24 hours (the specific yield of standard horizontal retorts under similar conditions is mere 15 kg of zinc).

A comparison of zinc distillation performance in horizontal and vertical retorts is given in Table 24.

Table 24

Comparative Performance of Zinc Distillation in Horizontal and Vertical Retorts (in terms of 1 ton of zinc)

Performance	Horizontal retorts	Vertical retorts
Fuel for heating and reduction (coal), t	2.22-2.39	1.54-1.71
Labour, man-hours	29-43	7.7-12.5
Recovery of zinc, %	86.4-87.8	90-94

A bar to extensive use of vertical retorts is the cost of carborundum, and the vertical retort technique is in use at some foreign plants, where local specifics make it advantageous.

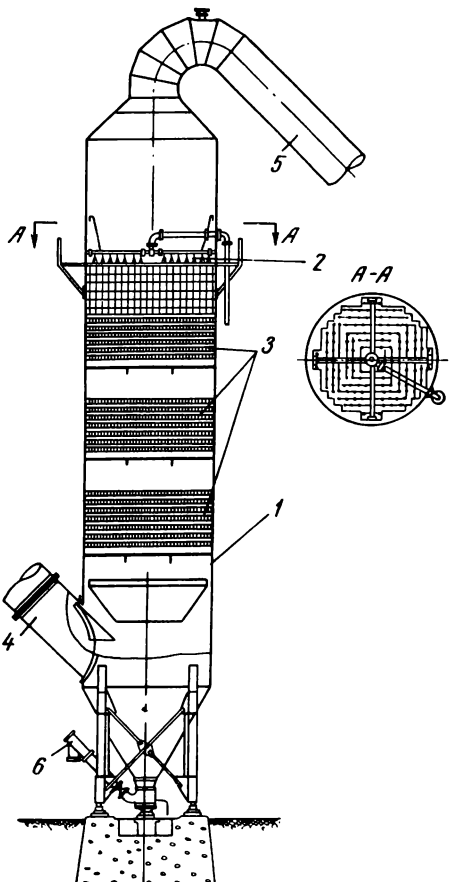


Fig. 70. Scrubber

1—casing; *2*—sprayers; *3*—packing; *4*—gas inlet; *5*—gas outlet; *6*—dust discharge device

From an engineering viewpoint, vertical retorts are much more perfect than the horizontal ones. Their opera-

tion is almost completely mechanized, however, the number of units in an average capacity plant, 15 to 20, is still great.

Distillation in electric furnaces. One of the shortcomings of vertical retorts is the necessity for transferring heat through walls which thus are heated to a higher temperature than the charge and so wear rapidly. This led to heating of the charge by a passing electric current and so zinc electrothermics developed.

By this latter method, zinc is manufactured in high shaft furnaces (12 to 14 m) built of high-grade refractory brick. Roasted concentrate is charged together with coke. Current is supplied by carbon electrodes spaced in height 8 to 10 m one from another and passes through the coke. Numerous electric arcs are thus struck between lumps of coke, and the charge is heated on the average to 1200°C. Zinc retort slag with 15-16% Zn is discharged continuously, while vapours of zinc are condensed to metal or oxidized, the oxide then being the final product. Besides zinc, zinc retort slag always carries lead, copper and noble metals, and, therefore, it requires additional treatment.

With the charge having some 42% of zinc latter's direct recovery attains 77-85%, electric power consumption being of the order of 2500-2900 kWh per ton of metal or oxide. Despite a relatively low temperature, service life of furnace walls is rather short, being about 100 days.

In an alternative technique, distillation is conducted in electric furnaces after a complete melting of the charge. Roasted concentrate is melted together with coal and fluxes at 1300-1350°C, resultant slag serving as a resistor body into which carbon electrodes dip (Fig. 71). In order to avoid overheating the slag with resultant damage to the furnace walls heat is partly supplied by an open arc of adequately high voltage.

Since the bath temperature is high, not only copper and zinc oxides, but iron oxides as well, are partly reduced even before the charge is completely melted. Iron dissolves carbon and copper, giving rise to a layer of cupferous cast iron. Overall recovery of zinc to gases attains 95%, but 4/5ths only are extracted as metal, the balance being dust and oxides.

Power consumption is higher than that in distillation from a solid charge, 3300 kWh per ton of zinc as compared to 2550-2900 kWh in the former method. Advantages of distillation of a molten charge are less stringent requirements upon starting materials and a more complex recovery of contained values.

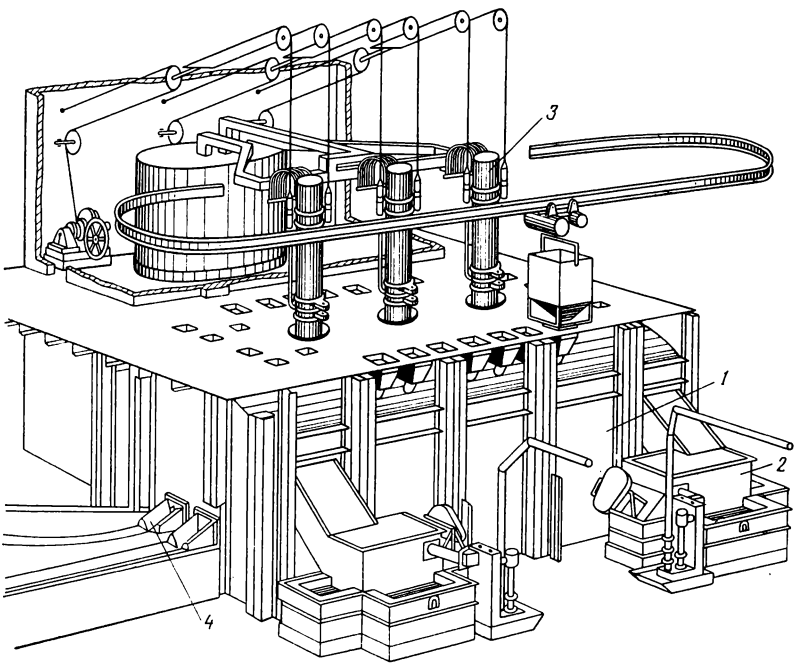


Fig. 71. Electric furnace for distillation of zinc
1—furnace; *2*—condensers; *3*—electrodes; *4*—cast iron and slag tapholes

It should be noted that cupferous cast iron finds industrial use, but recovery of noble metals from it is a problem.

As zinc electrothermics developed, condenser design was improved to allow condensation of the bulk of zinc to metal out of even relatively low-zinc gases. To this end, gases are sucked through a bath of molten zinc or passed through

a condenser where molten zinc is splashed by rotary impellers.

Greater surface area of molten metal enhances condensation of vapours even in greatly diluted proportions.

Zinc distillation in blast furnaces. In a standard lead reducing smelting, up to 4/5ths of zinc remain in the slag and the matte, the balance being lost with gases. In the lower zone of the blast furnace, where temperature is substantially higher than 1000°C, zinc is intensively reduced via reaction (163).

Zinc vapours react with CO_2 as they ascend the furnace shaft and settle as oxide on charge lumps, lower temperatures and higher CO_2 contents in the upper zone favouring the reaction

$$2CO \rightleftarrows CO_2 + C; \qquad CO_2 + Zn = ZnO + CO$$

At some plants, the lead smelting conditions are adjusted in a manner to obtain metallic zinc. The charge and coke are heated to 800°C before they are fed to the furnace, while blast is preheated to 600°C. The furnace is run at a high coke consumption with the effect that some 90% of zinc pass to vapours and are not oxidized. The gas temperature at the top is maintained at about 1000°C through combustion of a part of recycled condenser gas. Hot gases with 8-10% CO_2 and 5-6% zinc vapours enter large condensers where they cool sharply. In order to avoid condensation of zinc to dust, molten lead is sprayed inside condensers by rotary impellers. As it condenses on fine droplets of lead, zinc forms a lead-zinc alloy (2.26% Zn) which is continuously pumped away into a separate bath. The alloy cools there and separates into two layers, a bottom layer with 2.02% Zn, the balance, lead, and the top layer with about 99.5% Zn. The bottom layer is returned to condensers, while the top layer is refined.

Manufacture of 1 ton of zinc requires spraying inside condensers of some 400 tons of lead. In normal operation, up to 9/10ths of zinc are obtained from gases as molten metal, and 1/10th only, as powder and oxides. The latter are returned to the charge. Blast furnace slags contain 0.5% Pb and up to 5% Zn. A schematic diagram of the blast furnace with ancillaries is given in Fig. 72.

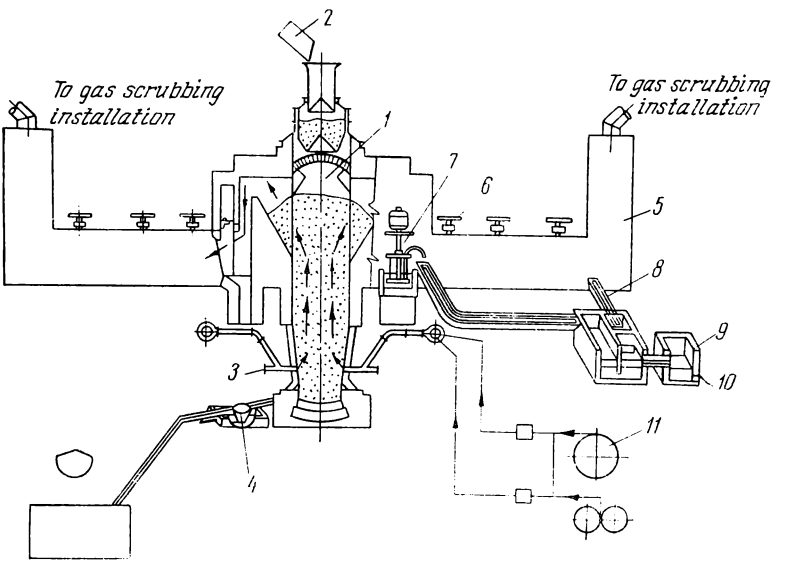


Fig. 72. Distillation of zinc in blast furnace

1—blast furnace with gas-tight charging arrangement; *2*—arrangement for charging hot sinter and coke; *3*—tuyeres; *4*—lead bullion tapping device; *5*—zinc condenser; *6*—impellers for spraying lead; *7*—pump for transferring alloy from condensers to separation bath; *8*—runner for returning lead to condenser; *9*—molten zinc receiver; *10*—zinc taphole; *11*—air heaters

Distillation of zinc in blast furnaces is an advanced treatment technique. However, it cannot be used for zinc concentrates hard to sinter.

Refining of Crude Zinc

Zinc from distillation generally carries the following amounts of impurities, %: 1-3 Pb; 0.03-0.5 Cd; 0.05-0.3 Fe; 0.05-0.1 Cu; 0.0003-0.05 As.

A cheapest and simplest refining of zinc by liquation is based on a reduction in solubility of impurities when zinc is cooled to 430-450°C. After settling for 24-36 hours, molten crude zinc separates into three layers: the bottom one contains up to 96% Pb, the middle one, composed of solid crystals of $FeZn_7$ carries the bulk of contaminating iron, while

the top layer is suitable in composition to a host of consumers since it contains not more than 1% Pb and 0.03-0.04% Fe and meets the specifications for zinc grades 2 and 3 (the USSR State Standard GOST 3640-65).

Crude zinc is liquated in reverberatory furnaces of up to 150 t capacity. Oxidation of zinc by furnace gases results in powder-like skimmings which are returned to distillation. Crude zinc is charged at regular intervals into the bath, and top settled layer is withdrawn as regularly. Waste that accumulates at the bottom is removed whenever necessary. Lead alloy is suitable for refining of lead (removal of noble metals), while the iron-bearing product is returned to distillation. This technique fails to remove cadmium which is thus lost with the zinc.

An alternative refining technique, redistillation, yields zinc of 99.996% purity and allows extraction of cadmium. Redistillation is a costly treatment, and demand for extra pure zinc is limited, and, therefore, we omit the description of its practice.

Hydrometallurgy of Zinc

Development of zinc distillation was paralleled, since 1915, by industrial introduction of a hydrometallurgical manufacture of zinc whose attractiveness was primarily in the possibility of obtaining a fairly pure zinc.

In hydrometallurgical treatment, zinc concentrates are also roasted, then leached by a diluted sulphuric acid. Zinc passes in solution according to reaction

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \qquad (164)$$

Silica and the bulk of iron oxides remain in the insoluble residue.

Resultant zinc sulphate liquor is treated for removal of impurities and processed by electrolysis. Pure zinc settles at the cathode, oxygen evolves at the anode and sulphuric acid that accumulates in the solution is suitable for leaching roasted concentrate, the overall reaction being

$$2ZnSO_4 + 2H_2O \rightleftarrows 2Zn + 2H_2SO_4 + O_2 + W \qquad (165)$$

The quantity of sulphuric acid given off in electrolysis should correspond to its consumption in calcine leaching. This balance is achieved by adjusting roasting conditions in a manner to leave some sulphur in the form of $ZnSO_4$ whose leaching requires no acid.

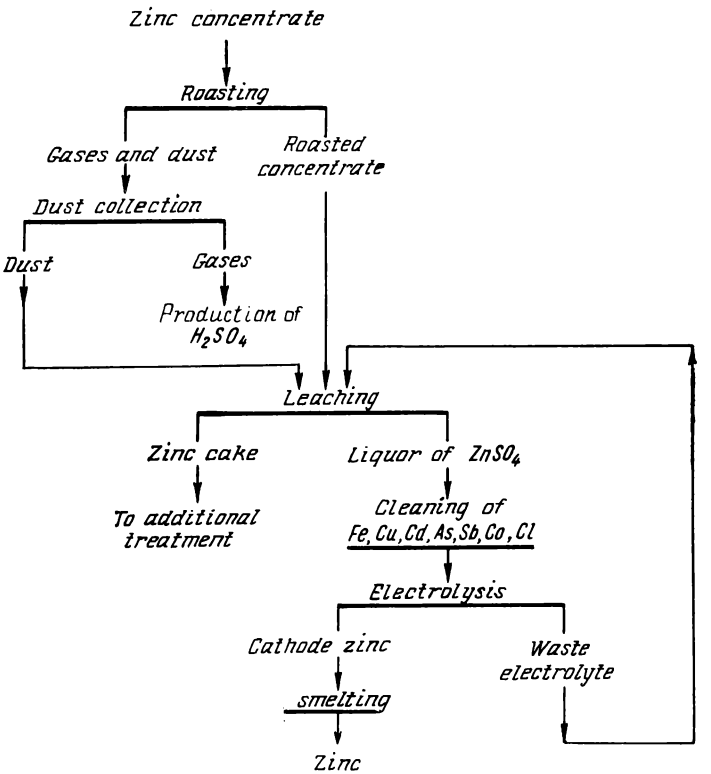


Fig. 73. Flowsheet for hydrometallurgical manufacture of zinc

Fig. 73 illustrates a flowsheet of hydrometallurgical manufacture of zinc which yields zinc in grades ЦВ, ЦО, Ц1 (GOST 3640-65) containing respectively 99.99, 99.975 and 99.95% of Zn.

38. Roasting of Zinc Concentrates

The chief reaction of zinc sulphide roasting (134) proceeds with the formation of SO_2.

Parallel with this, a proportion of sulphurous gas is oxidized, through catalytic action of metallic oxides, to SO_3

$$2SO_2 + O_2 \rightleftarrows 2SO_3 - 192.3 \text{ kj} \qquad (166)$$

$$K_p = \frac{P^2_{SO_3}}{P^2_{SO_2} \cdot P_{O_2}}$$

Sulphurous anhydride binds zinc oxide in a sulphate

$$ZnO + SO_3 \rightleftarrows ZnSO_4$$

In pre-distillation roasting, formation of a sulphate is undesirable as it tends to pass to sulphide and as such remains in the residual slag. From a hydrometallurgical viewpoint, the presence of small amounts of sulphates is indispensable. Formation of sulphates is favoured by high concentrations of SO_2 and O_2 in roasting gases and relatively low roasting temperatures. These are characteristic roasting conditions for zinc concentrates intended for subsequent hydrometallurgical treatment.

Zinc oxide is capable of interacting with Fe_2O_3 according to reaction

$$ZnO + Fe_2O_3 \rightarrow Zn(FeO_2)_2 \qquad (167)$$

Resultant zinc ferrite is readily reducible by carbon and in the distillation it presents no problem. By contrast, $Zn(FeO_2)_2$ dissolves slowly in diluted sulphuric acid and is lost with the insoluble residue, and, therefore, its formation is objectionable from hydrometallurgical standpoint.

Adjustment of roasting conditions has little effect on the fall of ferrites, and a best means to avoid their formation is to separate iron minerals in ore dressing.

Ignition point of ZnS depends on natural characteristics of the mineral concerned and its size, and for all practical purposes it may be assumed to lie between 550 and 600°C. Oxidation rate increases with the temperature, but the latter should be kept below a given value to avoid the risk of particles fusing together.

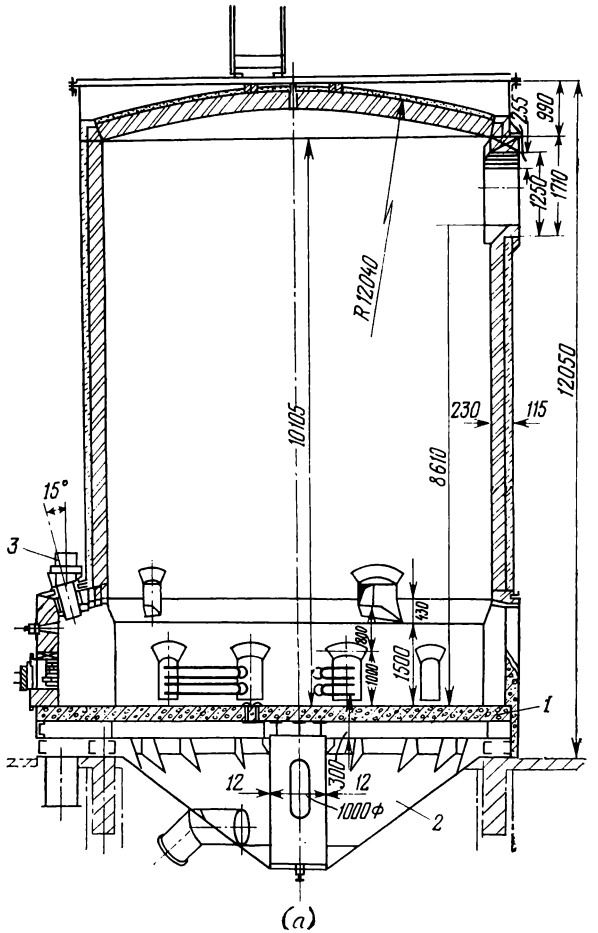
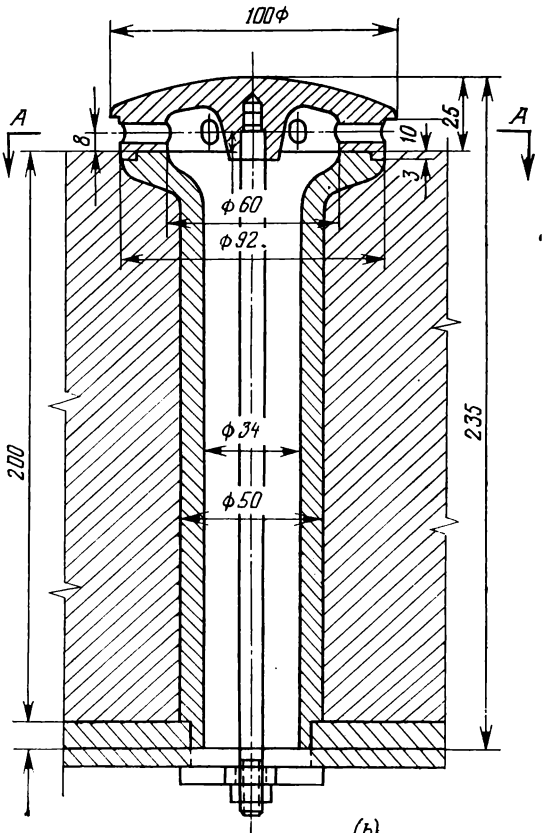


Fig. 74. Fluid-bed zinc

a—roaster; *1*—fluidized bed hearth; *2*—air box;



concentrate roaster

3—charging device; *b*—air nozzle

Other sulphide impurities oxidize to Fe_2O_3, Fe_3O_4, CuO, CdO, Sb_2O_3, As_2O_3, while lead turns to $PbSO_4$.

Oxides of arsenic and antimony are partly volatilized and partly oxidized to higher, less volatile oxides.

Oxidized minerals of barren rock vary little in chemical composition. They are merely calcinated, or their chemically bound water and carbon dioxide are removed.

Acid oxides: SO_3, As_2O_5, Sb_2O_5, Fe_2O_3, SiO_2 react with basic oxides and carbonates: FeO, CuO, PbO, ZnO and CaO and MgO, to give corresponding salts, sulphates, arsenates, antimonates, ferrites and silicates. Numerous reactions that are possible under these conditions generally fail to go to completion because of a lack of stoichiometric correspondence among reactants, poor mutual contact or low interaction rates. The chief roasting reactions are formation of zinc ferrites and of lead and zinc silicates. The latter interact with sulphuric acid in leaching to give off colloid silicic acid which hampers filtration and settling of pulps.

As early as 1950, zinc concentrates were still being generally treated in multi-hearth roasters. This is now practised by few smelters. In the USSR, all zinc concentrates are roasted in fluid-bed roasters (Fig. 74).

Fluid-bed roasters are prismatic or more frequently cylindrical in shape, 7 to 12 m high, 5 to 7 m in diameter and 20 to 40 m^2 in hearth area. Walls and roofs are lined with refractory brick, while hearth is built of heat-resistant concrete. Air blast is injected and uniformly distributed over the hearth area by nozzles.

Concentrate is fed to the roaster from one of the sides, and, forming a fluid bed, it flows over a lip on the other side into a discharge trough. Residence time of concentrate particles in the fluid bed is 10 to 12 hours. Finest particles are entrained by gases and fully roasted while in flight, their residence time inside the roaster being mere 5 to 20 seconds. Loss to entrained dust may be as high as 35% of the mass of the charge. Nine tenths of entrained dust settle in cyclones, and the balance, in electric precipitators downstream of them. Dust is well roasted and contains more sulphates than calcine, since temperature in dust collectors and flues is lower than that inside the roaster. Sulphuric acid

balance can thus be readily adjusted by varying the amount of dust fed out to leaching.

Heat evolving in sulphide roasting raises fluid bed temperature to 900-950°C. Excess heat is extracted by water coolers as form of steam suitable for power generation or other industrial use. Temperature inside the fluid bed and along the path of outgoing gases (inside dust collectors and flues) is automatically controlled to within ± 10°C. Concentrate feed and blast supply are also automatic. Pressure of outgoing gases along their path and contents of SO_2, SO_3 and dust are supervized either continuously or intermittently.

In pre-distillation roasting, the temperature is about 1100°C. The charge is roasted in two steps, the second step is sintering machines, the process yielding a sulphur-free sinter.

Concentrates for fluid-bed roasting may carry a high moisture and be fed to roasters even in the form of pulp.

A major advantage of fluid-bed roasting in application to hydrometallurgy of zinc is a somewhat lesser formation of ferrites and silicates, since the possibility of contact between oxides of zinc, silicon and iron is by far lower than that in multi-hearth roasters.

For equal size, a fluid-bed roaster is more than 3 times more productive than a multi-hearth roaster. A fluid-bed roaster 6.5 m in diameter processes 150 t of concentrates in 24 hours. Specific capacity, or the ratio of the quantity of materials roasted in 24 hours to the surface area of the fluid-bed, attains 5 t/m^2 over 24 hours.

Specific capacities of multi-hearth and fluid-bed roasters can readily be compared from the data below:

t/m^2 hearth area	Multi-hearth roasters 0.18-0.24	Fluid-bed roasters 3.5-6.0
t/m^3 of roaster volume	0.2	0.4-0.8

Owing to a high rate of oxidation of sulphides in a fluid bed, the materials can be roasted at small excesses of air and higher SO_2 concentrations, 8-10%, in gases instead of 4-7% obtainable in multi-hearth roasters. Even greater concentrations can be attained by increasing specific capacities of roasters through blast oxygenation, which is restricted by some practical problems.

Experiments in blast oxygenation have shown a possibility for increasing roaster specific capacity to 6.5 t/m² 24 h, resultant SO_2 content being brought to 9.6%, and dust losses being reduced from 38 to 19% of the mass of the charge.

Calculation of Roaster Gas Composition

Sphalerite oxidizes according to reaction

$$ZnS + 1.5O_2 \rightarrow ZnO + SO_2$$

Oxidation in pure oxygen at latter's theoretical consumption yields a 100% sulphurous gas.

Air contains, per mole of O_2, 79 : 21 = 3.76 moles of N_2. Oxidation of 1 mole of sphalerite in the air results in roaster gases that carry $1.5 \cdot 3.76 = 5.64$ moles of N_2 and 1 mole of SO_2. Content of SO_2 is

$$\frac{1}{1+5.64} \cdot 100 = 15.5\%$$

For an excess of air of $\alpha = 1.5$ roaster gases will carry additionally:

oxygen: $1.5 \cdot 0.5 = 0.75$ mo e;
nitrogen: $0.75 \cdot 3.76 = 2.82$ moles.

Content of SO_2 will amount to

$$\frac{1}{1+5.64+2.82+0.75} = 9.77\%$$

When blast is oxygenated to, e.g., 35% (at an air excess of $\alpha = 1$), each mole of oxygen is accompanied by 65 : 35 = 1.86 moles of nitrogen, and roaster gases will contain a following percentage of SO_2

$$\frac{1}{1+1.5 \cdot 1.86} = 26.4\%$$

39. Leaching of Roasted Concentrates

As the phase composition below shows, a mixture of roasted concentrate (calcine) and recycled dust carries a plurality of zinc compounds and other components, whose con-

tents are, %:

ZnO	$ZnSO_4$	Zn_2SiO_4	ZnS	$ZnFe_2O_4$	$PbSO_4$	$PbSiO_3$	Fe_2O_3
75.1	4.4	0.8	1.7	2.0	1.2	0.8	8.5

Fe_3O_4	$CaSO_4$	$MgSO_4$	Cu_2O	CdO	Undetermined
1.5	1.2	1.2	1.3	0.3	1.0

The undetermined include, among others, salts of iron and calcium formed by arsenic and antimonic acids. Calcine is often reported to carry free FeO. However, the latter's presence is highly improbable after an oxidizing roast because of its great chemical activity and favourable conditions for binding it into ferrites and silicates.

A spent electrolyte, used for leaching at a temperature of about 35°C, generally carries from 130 to 160 gram/litre H_2SO_4 (1.3-1.6 mole/litre) and 100-125 gram/litre Zn^{2+} (0.6-0.78 mole/litre).

Under these conditions, zinc oxide readily turns to be a soluble sulphate according to reaction (164) whose rate is controlled by the diffusion of sulphuric acid to the surface of solid particles, and, additionally, when $ZnSO_4$ rises sufficiently, by the removal of the latter into the body of the solution.

Diffusion is favoured by stirring the pulp and heating it to 50-60°C at the expense of exothermic reactions.

In that sulphide zinc and ferric oxide do not go to the solution while Fe_3O_4 interacts with sulphuric acid according to reaction

$$Fe_3O_4 + 4H_2SO_4 = Fe_2(SO_4)_3 + FeSO_4 + 4H_2O \qquad (168)$$

Ferrite and sulphide zinc goes in solution at a relatively low rate and generally incompletely by way of reactions

$$ZnFe_2O_4 + 4H_2SO_4 \rightarrow ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O \qquad (169)$$

The rate of reaction (168) is controlled by chemical kinetics, and can be increased by raising the acidity and/or the temperature only of the solution.

Roasting at high temperatures, on the face of it, should promote greater ferrite-formation and thus reduce the transfer of zinc to solution. However, practical data tend to indicate that, on the contrary, zinc leaching improves, pro-

bably, because of a ferrite disproportionation

$$2ZnFe_2O_4 \rightarrow ZnO + ZnFe_4O_7 \quad (170)$$
(*solid solution*)

The iron oxide Fe_3O_4 dissolves slowly and incompletely, a greater proportion of it goes to the residue together with lead and calcium sulphates.

Sulphuric acid and iron, lead and calcium arsenates and antimonates give $PbSO_4$, $Fe_2(SO_4)_3$ and $CaSO_4$, as well as probably, polyarsenic acids, as $As_2O_5 \cdot 4H_2O$ or $3As_2O_5 \cdot 5H_2O$ (or, respectively, H_8AsO_9 and $H_{10}As_6O_{20}$)* and relatively poorly soluble antimonic acids generally described by the formula $Sb_2O_5 \cdot nH_2O$.

Silicates of zinc, lead and iron are decomposed by sulphuric acid with evolution of $H_2SiO_3 \cdot nH_2O$ which renders difficult subsequent settling and filtration of pulps

$$Me_2SiO_4 + 2H^+ + (n-1)H_2O \rightarrow Me^{2+} + H_2SiO_3 \cdot nH_2O \quad (171)$$

Ion Pb^{2+} is bound in a poorly soluble $Pb(HSO_4)_2$.

Copper protoxide dissolves but partly, giving off a metallic deposit (90).

Oxides of bivalent copper, cadmium and cobalt are almost completely transferred to solution. These impurities hamper subsequent electrolysis, and, therefore, liquors require purification.

Iron can be removed simultaneously with leaching. Ions Fe^{2+} are oxidized by manganese dioxide

$$2FeSO_4 + MnO_2 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + 2H_2O \quad (172)$$

Subsequent hydrolysis of Fe^{3+}, which takes place according to reactions (101), becomes feasible toward the end of leaching, when the acid is almost completely spent for the solution of ZnO and other impurities. At the same time, reaction (172) calls for an acid medium, and it should be carried out at the beginning of leaching.

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* A. N. Kargintsev, L. N. Trushnikova, V. G. Lavrentjeva, Solubility of Non-Organic Substances in Water, Leningrad, 1972.

Removal of iron from liquor is paralleled by that of arsenic, antimony and partly of silicic acid. Arsenic and antimony can be effectively settled out together with iron, if latter's content is greater by a factor of 10-20 than that of arsenic and by a factor of 20-40 than that of antimony. To this end, the lacking iron is sometimes added to the solution.

Adequately full recovery of zinc requires excess sulphuric acid, but removal of iron calls for a neutral medium at the end of leaching. Therefore, leaching is conducted in two steps. First, roasted zinc concentrate is treated by a previously obtained weakly acid solution of $ZnSO_4$ that contains 100-130 gram/litre of zinc and 1-5 gram/litre of free sulphuric acid. This acidity is inadequate to leach all of the zinc, and part of it passes to solution which thus becomes neutral, and, therefore, pure as regards iron. After the neutral leaching, the insoluble residue carries much zinc, and, therefore, it is leached for a second time by a spent electrolyte with about 150-170 gram/litre H_2SO_4. At the end of acid leaching, the concentration of sulphuric acid in the liquor falls to 1-5 gram/litre, the liquor is separated from the deposit and transferred to neutral leaching (Fig. 75).

A two-stage leaching is advantageous in large scale manufactures with fairly constant compositions of raw materials and is carried out as a continuous process.

Some plants prefer batch-leaching in which a calculated amount of cooled fine calcine is fed to a mixing apparatus together with pyrolusite MnO_2 required to oxidize iron according to reaction (172) and treated by recycled acid solution. H_2SO_4 concentration in the latter falls off in two hours from 60-70 gram/litre to 2-6 gram/litre. Next, calcine is added in small portions over a time interval of 30 minutes, while stirring the batch, to raise pH factor to 5.2-5.5 after which the pulp is transferred to thickening, the resultant liquor being filtrated, purified and treated by electrolysis, as shown in flowsheet in Fig. 75.

In roasting, calcine tends to fuse. Large fused aggregates of sulphide, ferrite and silicate particles react slowly with sulphuric acid. Transfer of zinc from coarser particles is rather slow, as compared to that from finer grains, since the surface of zinc compounds is often isolated from the

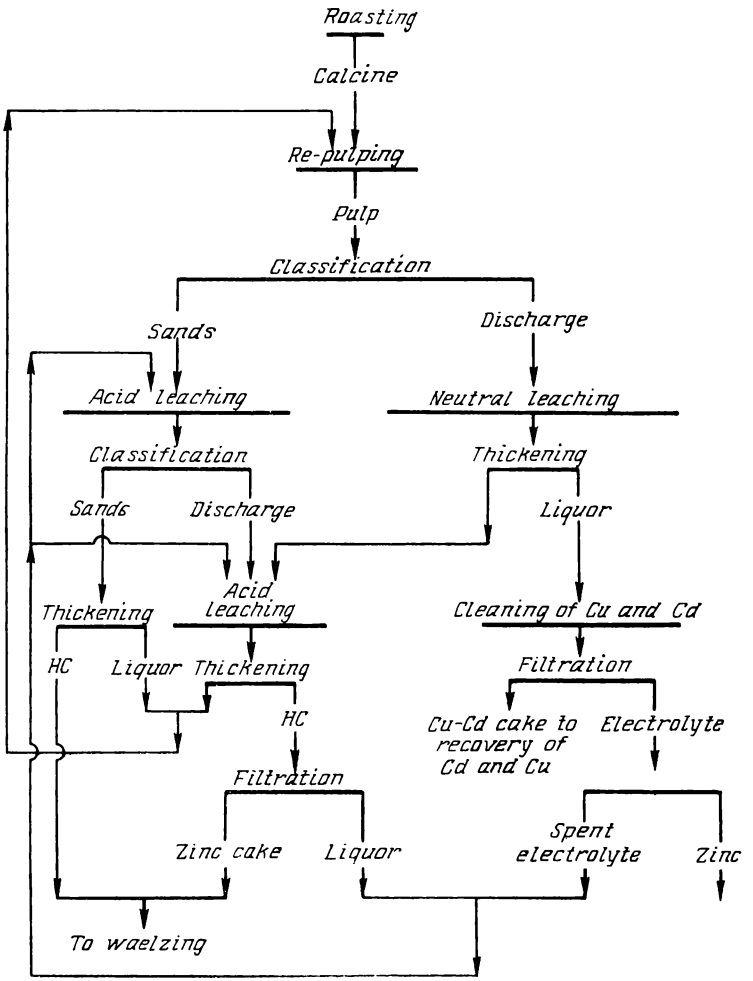

Fig. 75. Flowsheet for continuous leaching of calcine

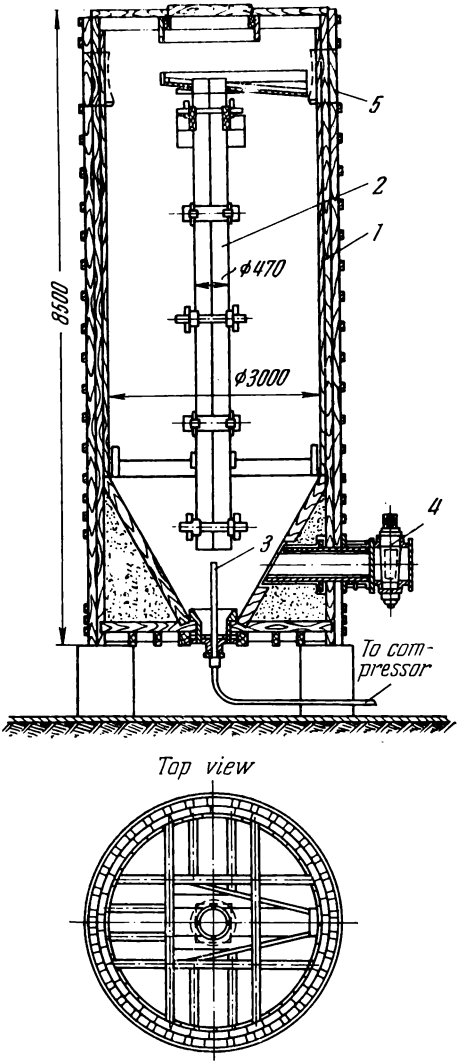

Fig. 76. Pneumatic agitator (Pachuka tank)

1—vat with conical bottom; *2*—central pipe; *3*—compressed air nozzle; *4*—pipe for complete discharge of pulp; *5*—outlet for pulp flow to a downstream series agitator

liquor by barren rock. It is good practice, then, to grind coarse grains (sands) prior to leaching.

In continuous leaching, hot calcine is discharged continuously from the roasters into launders where it mixes with a stream of liquor and is carried by the latter to classifiers. Subsequent separate leaching of overflow and sands is illustrated in flowsheet of Fig. 75.

Some plants, which practise batch-leaching, prefer to cool the calcine and classify it in vibrating screens. Coarse fractions are ground and returned to roasting.

Leaching requires effective stirring of pulp to keep solid particles in suspension. Pneumatic and mechanical apparatus are used to this end. In the former, the pulp is agitated by compressed air, and in the latter, by a rotary stirrer.

A pneumatic stirrer (agitator) (Fig. 76) has already been described in Para. 19. It is simple as to design and cheap in operation, but its shortcoming is that the liquors are cooled by the agitating blast.

A mechanical agitator is shown in Fig. 77. Its tank is of steel sheets protected by acid-resistant brick. At the centre, a rubber-lined pipe with perforated walls houses an impeller which rotates at 40 to 100 rpm. The impeller produces a downward flow of pulp which is sucked in through holes, this ensuring circulation of pulp inside the tank. Stirring in mechanical agitators is better than that in pneumatic ones, the pulp they contain can be heated by steam circulating inside the lead coiled pipes, but mechanical stirring consumes more power. Pneumatic agitators are particularly suited for continuous leaching, while mechanical ones, for batch leaching.

Continuous leaching is carried out in three or four pneumatic agitators connected in series. One such battery serves for neutral, and another one, for acid leaching.

At the completion of neutral leaching, iron oxides sulphate hydrolyzes in the tail agitators with the formation of insoluble basic salts. Compounds of arsenic and antimony are removed with the deposit from the solution.

From an end agitator pulp enters thickeners of the neutral strand (see Para. 9), clarified overflow is transferred to other apparatus for removal of impurities. Thickened product, insoluble residue of neutral leaching in the form of

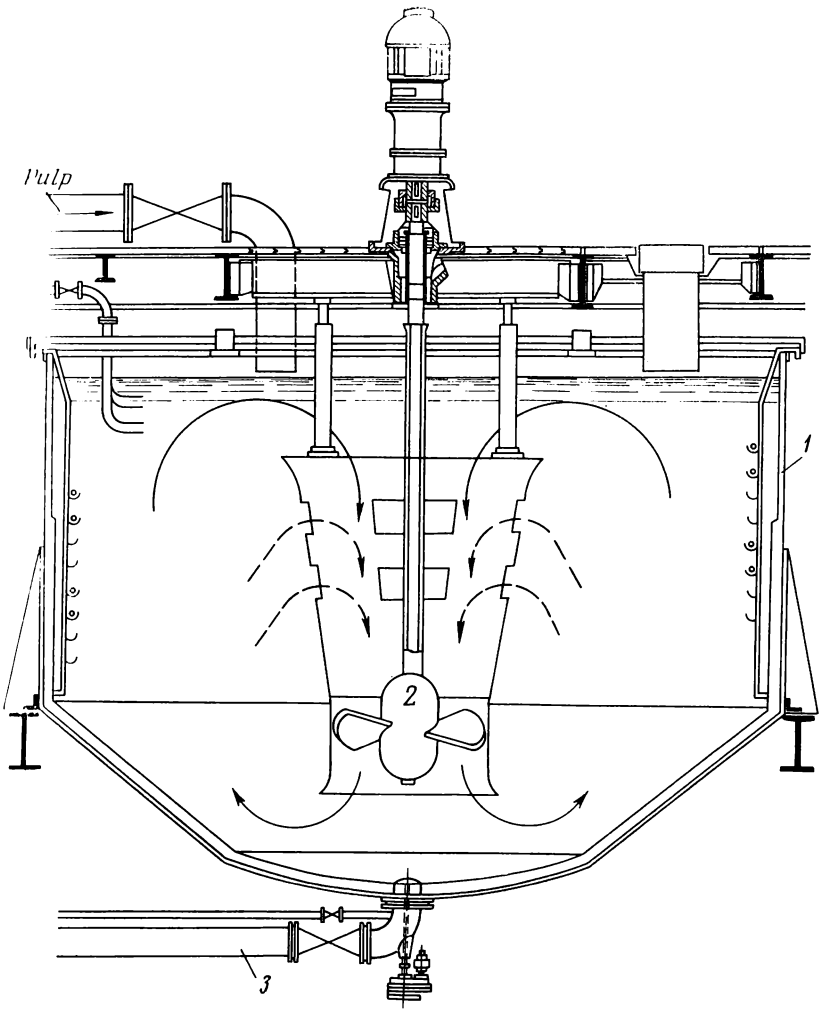

Fig. 77. Mechanical agitator

1—tank with coiled pipe for heating pulp; *2*—impeller stirrer; *3*—pulp outlet pipe

a thick pulp with 15-20% solids and 80-85% (by mass) of neutral liquor, is leached by spent electrolyte that contains 40-60 gram/litre Zn and 90-160 gram/litre H_2SO_4. At the beginning of leaching, solids-to-liquid ratio is 1-to-10 of the pulp, and when the process is completed the ratio falls to 1-to-20 as a result of solution of zinc.

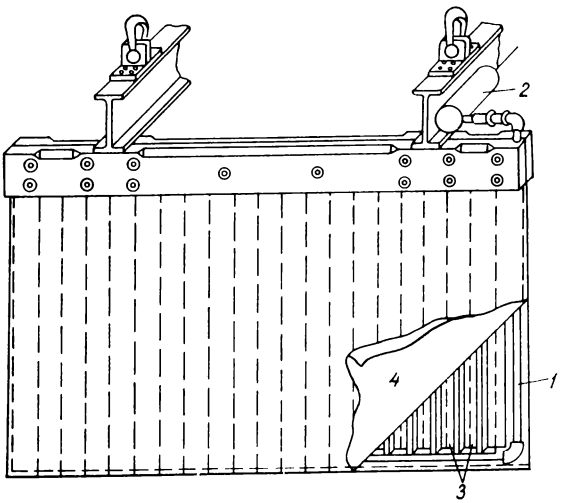

Fig. 78. Intermittent-action Moore filter
1—frame built of pipes; *2*—filtrate header; *3*—wooden planks; *4*—jacket of cloth

Pulp temperature, which is 40-50°C at the beginning, rises to 50-60°C at the end of acid leaching at the expense of exothermic reactions between oxides and sulphuric acid.

The pulp then enters thickeners of the acid strand which operate similarly to neutral thickeners. The product is filtered, washed and taken out of the manufacture circuit as waste zinc cake which carries about 1/10th of the starting amount of zinc and some lead, gold, silver, cadmium, copper and germanium. Subsequent processing of zinc cake is discussed below.

Before zinc cake is removed from the production circuit it should be separated from the solution and thoroughly washed, since more than half of it is a liquor rich in zinc.

The cake should be washed with a minimum of water to avoid its amount exceeding that used for leaching. Particularly suitable for washing of deposits by small amounts of water are intermittent-action Moore (or Butters) filter.

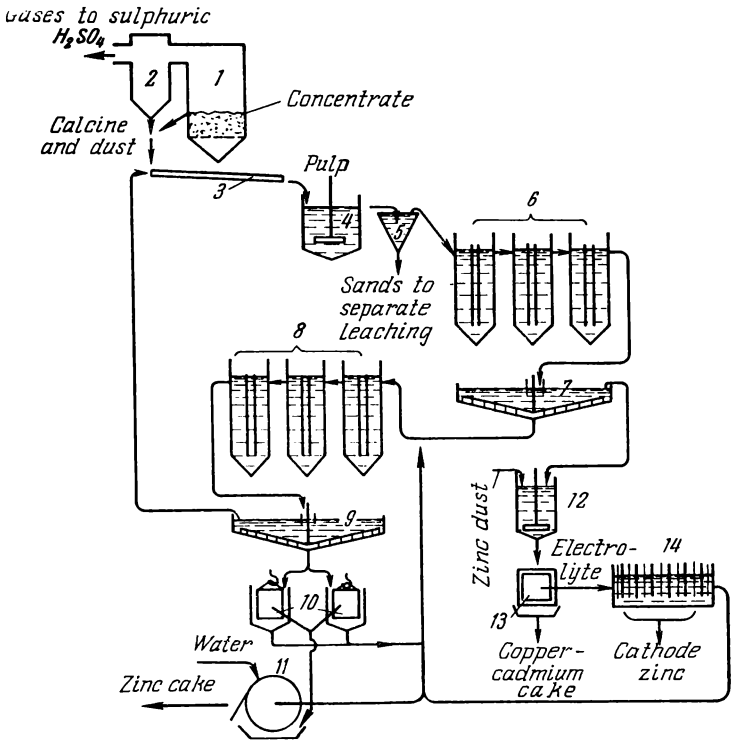

Fig. 79. Flowsheet for hydrometallurgical manufacture of zinc

1—roaster; *2*—dust collectors; *3*—runner; *4*—tank with stirrer; *5*—classifiers; *6*—neutral agitator tanks; *7*—neutral thickeners; *8*—acid agitator tanks; *9*—acid thickeners; *10*—intermittent-action Moore filters; *11*—disk-type vacuum-filters; *12*—tanks for precipitation of copper and cadmium; *13*—filter press; *14*—electrolytic cells

A Moore filter consists of 10 to 30 frames (generally termed leaves) suspended parallel to one another on I-beams (Fig. 78). A frame is built of copper pipes and may measure, e.g., 2.5 × 3.0 m. The walls of pipes that are oriented inside the frame are perforated. One end of the pipe is

plugged, and the other end branches off a header which in its turn, connects all frames (leaves) of the filter to a vacuum pump. Wooden planks are placed inside the frame, and the latter is jacketed in a filtering cloth. An overhead crane immerses a set of frames into a pulp tank. The vacuum pump causes the liquor to percolate through the cloth pores and to pass via the header into a receiver, a 30- or 40-mm thick cake being deposited on the outside surface of the cloth. An overhead crane then transports the filter to a tank with water, while compressed air is supplied into the header, and the cake is thus dislodged into water. Once mixed, the pulp is refiltered in drum or disk-type vacuum-filters (see Para. 9).

Acid thickener overflow together with filtrates from frame (Moore), drum or disk-type filters and washing waters is circulated to neutral leaching (Fig. 79).

Calculation of the Yield and the Composition of Zinc Cake

Roasting of a concentrate of the following average composition: 54% Zn; 2% Pb; 1.0% Cu; 0.2% Cd; 30% S; 2% SiO_2; 9.0% Fe; 0.3% Al_2O_3; 1% CaO; 0.5% MgO, resulted in a calcine with 0.5% sulphide sulphur (S_S) and 2% sulphate sulphur (S_{SO_4}). Calculate the phase composition of the calcine and the yield of zinc cake.

Having divided the analysis data by respective atomic masses, we express the concentrate composition in kg-atoms per 100 kg: 0.827 Zn; 0.010 Pb; 0.016 Cu; 0.002 Cd; 0.937 S; 0.033 SiO_2; 0.161 Fe; 0.003 Al_2O_3; 0.018 CaO; 0.013 MgO.

Assuming that in roasting metals have formed oxides only, and sulphur has been completely oxidized, we obtain:

	ZnO	PbO	CuO	CdO	SiO_2
kg-atom	0.827	0.01	0.016	0.002	0.033
kg	67.3	2.2	1.3	0.3	2.0
	Fe_2O_3	Al_2O_3	CaO	MgO	Total
kg-atom	0.081	0.003	0.018	0.013	—
kg	13.0	0.3	1.0	0.5	87.9

Actually, the calcine carries 0.5% of S_S which replaces oxygen and thus gives an additional mass equal to $\frac{32-16}{32} \cdot 0.5 = 0.25\%$. Expressing S_{SO_4} in terms of SO_3, we obtain $2 \cdot \frac{80}{32} = 5\%$.

This taken into account, the amount of calcine will be

$$\frac{87.9}{94.75} \cdot 100 \approx 93 \text{ kg}$$

The calcine will carry

$$\frac{0.5 \cdot 93}{100 \cdot 32} = 0.015 \text{ kg-atom } S_S$$

and

$$\frac{2 \cdot 93}{100 \cdot 32} = 0.058 \text{ kg-atom } S_{SO_4}$$

Having assumed that sulphide sulphur is bound in ZnS, and the sulphate sulphur, in $PbSO_4$, $CaSO_4$ and $ZnSO_4$, and all of the iron, in $Zn(FeO_2)_2$, the phase composition of the calcine can readily be calculated, kg-atom:

$PbSO_4$		0.010
$CaSO_4$		0.018
$ZnSO_4$	0.058	0.018
ZnS	$-(0.01+$	$0.015) = 0.030$
$Zn(FeO_2)_2$		0.081
ZnO	$0.827-(0.030+$	$0.015+0.081) = 0.701$
CuO		0.016
CdO		0.002
SiO_2		0.033
Al_2O_3		0.003
MgO		0.013

Proceeding from the substances that fail to go in solution in leaching (printed in bold type), we obtain the phase composition of the zinc cake

	$PbSO_4$	$CaSO_4 \cdot 2H_2O$	ZnS	
kg-atom	0.010	0.018	0.015	
kg	3.0	3.1	1.5	
	$Zn(FeO_2)_2$	SiO_2	Al_2O_3	Total
kg-atom	0.081	0.033	0.003	—
kg	19.5	2.0	0.3	29.4

Actual plant cakes from disk-type filters, have a moisture of about 30%. After drying at 105°C, they still carry about 5% of non-washed-off zinc sulphate. In terms of $ZnSO_4 \cdot 7H_2O$, this will amount to

$$5 \cdot \frac{287.4}{65.4} = 22\%$$

The quantity of dry cake will be

$$\frac{29.4 \cdot 100}{78} = 38.7 \text{ kg}$$

Therefore, there will be

$$\frac{(0.015+0.081) \cdot 65.4}{38.7} = 16.2\%$$

of insoluble zinc in the dry cake.

The amount of soluble zinc will then be 5%, and its total, 21.2%.

Loss of zinc with cake in per cent of that in the starting concentrate will be

$$\frac{21.2 \cdot 33.7}{54} = 15.2\%$$

Lead in the cake, %, will be

$$\frac{0.01 \cdot 207}{38.7} = 5.3\%$$

Besides, zinc cakes carry about 1% Cu, 0.2% Cd, gold, silver and germanium. Therefore, their treatment for recovery of values thus becomes readily apparent.

Zinc cake processing. Zinc cakes may be treated by waelzing* in rotary kilns, similar in design to those used for burning bauxites or calcinating alumina (see Fig. 94). Kiln length is 40 to 60 m, and its diameter, 2 to 3.5 m.

Before the cakes are charged, they are dried, ground and mixed with coke fines that serve as reducer.

As it slides down the kiln, the charge gradually heats to 1100-1300°C by countercurrent combustion products from burning of fuel oil or natural gas.

Oxides and ferrites of lead, zinc and cadmium are reduced, to form vapours of metals, as,

$$ZnO + CO \rightleftarrows Zn + CO_2$$

Metal vapours are oxidized by kiln gases and entrained by them as fine particles of solid oxides. Sublimates are collected in sleeve filters and contain, %: 40-65 Zn; 5-8 Pb; 0.3-0.4 Cd.

Next, sublimates are leached by sulphuric acid and processed similarly to zinc concentrates, but in separate apparatus since they carry a sizable amount of impurities.

Solid residue from waelzing, clinker, is smelted in blast furnaces to copper-lead matte which concentrates gold and silver.

40. Removal of Impurities from Neutral Zinc Sulphate Liquor

Copper, cobalt, iron, arsenic and antimony when present even in small amounts greatly lower current efficiency. Some ions, e.g., nickel and cobalt, give rise to rough and

* From the German, wälzen, or to roll.

porous deposits whose subsequent smelting results in substantial oxidation and loss of zinc.

All the above metals are frequently carried by zinc concentrates and in leaching pass, to various extent, to solution. Approximate data on the composition of non-purified neutral solutions and present-day requirements upon the composition of the electrolytes are given in Table 25.

Table 25

Approximate Data on Composition of Non-Purified Neutral Liquors

Impurities	Content, gram/litre			
	approximate			required at current density of 500 A/m²
	liquor 1	liquor 2	liquor 3	
Cd	0.35	0.15	0.25	0.002-0.004
Cu	3.0	0.3	0.6	0.0001-0.0002
Fe	0.03	0.03	0.002	0.02-0.05
As	—	0.03	0.001	0.0001
Sb	—	0.001	0.001	0.0001
Co	0.003	0.001	0.07	0.002-0.004
Ni	0.001	—	0.003	0.0005-0.001

The neutral liquor is continuously cleaned of Cu and Cd prior to electrolysis. Removal of cobalt and chlorine is not always required. Cobalt and chlorine are extracted from a portion of electrolyte (temporarily removed from the circuit) in order to avoid their accumulation above a given level.

Contaminating salts of alkali metals, magnesium, manganese (divalent), aluminium and other soluble sulphates gradually accumulate in the circulating liquor and lower $ZnSO_4$ solubility. Latter's crystallization is prevented by keeping aggregate content of above salts below 30 gram/litre.

Removal of copper and cadmium is based on the cementation reactions.

$$Cu^{2+} + Zn \rightarrow \downarrow Cu + Zn^{2+}$$

$$Cd^{2+} + Zn \leftarrow \downarrow Cd + Zn^{2+}$$

To speed up purification, zinc is introduced in the form of a powder obtained by atomization of molten metal or condensation of its vapours ("zinc dust").

Zinc dust consumption exceeds the stoichiometric amount as it dissolves partly because of the reduction of hydrogen ions. Besides, copper and cadmium that precipitate on dust particles interfere with its efficient utilization (see Para. 2).

Liquors are cleaned of copper and cadmium in tanks 35 to 45 m^3 in capacity with paddle stirrers. The tank is filled

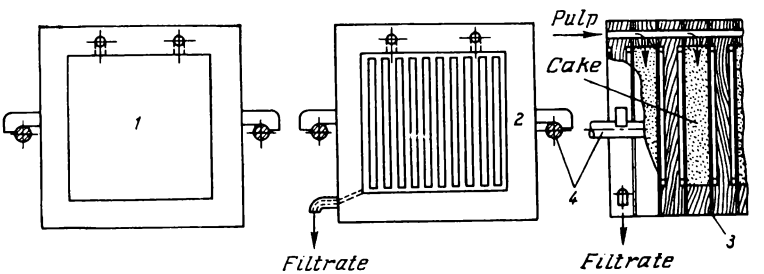

Fig. 80. Components of plate-and-frame filter-press
1—frame; *2*—plate; *3*—filter cloth; *4*—bed guide rail

with a neutral liquor from neutral strand thickeners, and, after zinc dust is added, is agitated for 50-40 minutes at 50-60°C. Resulting precipitate is filtered in pressure filters (Fig. 80). The above contaminants may also be removed in apparatus similar to conical cementation reactors (Para. 19) where dust powder particles are caused to float by the circulating liquor as if in a fluid bed.

Filter presses (or pressure filters) are batch-type apparatus that require manual disassembly for discharge of deposited cake. Therefore, they may find advantageous use for filtering of small amounts of solids from large quantities of liquid only.

A filter press is assembled of two kinds of components, plates and frames in a bed provided with two parallel guides (steel rails). A plate is a rectangular piece of wood, metal or plastic, 20-50 mm thick, provided in its middle portion with parallel grooves that branch into small troughs at their ends. Overall dimensions of the frames are the same

as those of the plates. One of the plate side walls is provided with a hole and a stopcock for discharging filtrate. At their tops, the frames and the plates carry 2 to 4 round holes. In the frames, these holes communicate with the internal space. Frames and plates alternate on the bed, a filtering cloth being inserted between each frame and plate. When the filter is assembled, the round holes register to form a cylindrical canal, and corresponding holes are cut in the cloths. A set of 10 to 60 frames and plates each is clamped together by a power screw or a hydraulic device. Pulp to be filtered is supplied by a pump at a pressure of 147.2-392.4 kN/m^2 (1.5-4 atm) into cylindrical canals and passes into the frames inside a narrow space between two parallel filtering cloths. Liquor that passes through cloth pores is withdrawn via the plate grooves and trickles to a collecting trough. Once the filter is full of cake, it is disassembled, and the cake, discharged.

The above batch purification of liquors is low in productivity, requires a high consumption of zinc dust and gives low-concentration precipitates because of excess zinc.

A modern continuous purification technique consists of two stages. First, copper is settled out in three agitators, arranged in series. The first agitator is charged with an amount of zinc dust theoretically required to bring Cu^{2+} content down to 50-200 milligram/litre, and copper cake is separated by thickening or in pressure filters, while the filtrate is continuously circulated through a second similar battery of agitators, where zinc dust is fed to the first agitator only. Prior to filtration, the pulp is sometimes cleaned in hydrocyclones, the coarser fraction of the sands, that is collected there and consisting chiefly of zinc, is recycled to the first purification stage.

Co^{2+} may be simultaneously settled out in the first step of cementation by adding sodium thioantimonate $Na_3SbS_4 \cdot 9H_2O$ in a ratio of Sb : Co = 1. The action of this additive consists, presumably, in a formation in the course of cementation of a corrosion-resistive cobalt-antimony-sulphur alloy instead of pure cobalt.

The technique is similar to a well-known copper-antimony cleaning method involving the addition of copper sulphate and antimonic acid, notwithstanding the risk of

a lethal hydrogen arsenide evolving, to ensure greater cementation of cobalt. It is also common knowledge that cobalt cementation is promoted, similarly to thioantimonate, by sodium sulphite Na_2SO_3 which is reducible by zinc to S^{2-} and is capable of sulphidizing cobalt or its alloy with copper.

A copper-cadmium cake consists of copper, cadmium, excess zinc dust and solid particles of barren rock entrained by the neutral liquor out of thickeners, its chemical composition being, %: 2-8 Cu; 6-12 Cd; 30-40 Zn. The copper-cadmium cake is used to manufacture cadmium and to recover copper as a by-product. Thallium also tends to concentrate in the copper-cadmium cakes.

At regular intervals, a portion of the electrolyte is bled out of the circuit to remove cobalt and chlorine. Cobalt is removed with the deposit that is settled out by additions of sodium xanthate and copper sulphate. Cobalt content in the liquor can readily be lowered to 4 milligram/litre. Cobalt cake with about 4% Co is used for the manufacture of the metal (Para. 27).

Chlorine is removed from liquors as it accumulates above a 100 to 150 milligram/litre mark. Liquors may be contaminated by chlorine from mains water supply or recycled matter. In electrolysis, chlorine ions cause intensive corrosion of lead anodes, thus contaminating the deposit with lead. Presence of chlorine also explains rapid decay of coiled pipe coolers. Chlorine is settled out as CuCl by mixing the liquor with newly-settled cementation copper in the presence of copper sulphate.

41. Electrolytic Deposition of Zinc

Reactions at the Electrodes

Treated by electrolysis is a purified neutral zinc sulphate liquor of pH of about 5, containing, however, small amounts of elements listed in Table 25 and up to 10 gram/litre of Mn^{2+}.

As mentioned, electrolysis of zinc can be described by reaction (165) which makes readily apparent that as zinc plates out at the cathode, free sulphuric acid accumulates

in solution. All baths are supplied with electrolyte in parallel, with the effect that zinc concentration and acidity average values are the same in each of them. To obtain adequate current efficiency, acid concentration-to-zinc ratio in the liquor should not be too high, as its increase brings closer together the equilibrium potentials for zinc and hydrogen (in accordance with the Nernst equation) and thus lowers zinc electrolysis current efficiency.

Another precondition of a successful electrolysis is a high hydrogen overvoltage at the zinc cathode which depends on electrolyte temperature and current density.

Therefore, high current efficiencies require the electrolysis to be conducted in concentrated zinc sulphate solutions, at large current densities and low temperatures.

The reactions below are probable at the lead anode of the electrolysis cell

$$Pb + SO_4^{2-} - 2e \rightleftarrows PbSO_4; \qquad E^\circ = -0.36 \text{ V};$$
$$Pb + 2H_2O - 4e \rightleftarrows PbO_2 + 4H^+; \quad E^\circ = +1.45 \text{ V}$$

Standard potential values involved tend to indicate that the anode is the site of, first of all, formation of lead sulphate which coats the anode in a thin film of poorly soluble crystals. Open surface of lead thus decreases, current density goes up, as does the anode potential. Next, PbO_2 settles out in the pores of the lead sulphate film, then a fresh increase in anode potential causes evolution of oxygen according to reaction (24), which is the chief anode process.

A substantial part in the anode process is that of Mn^{2+} which oxidizes according to reaction

$$Mn^{2+} + 2H_2O - 2e^- \rightarrow MnO_2 + 4H^+; \quad E^\circ = 1.23 \text{ V} \quad (173)$$

Anode surface is coated by loose slime from hydrous manganese dioxide MnO_2H_2O which is suitable for oxidation of iron in purification of liquors (172).

Power Consumption

Power consumption in zinc electrolysis is higher than that in the previously discussed electrolytic refining of copper and nickel. Work produced by the electric current is consumed not only for the transfer of ions through the

electrolyte, but for the chemical reaction as well. Irrespective of this, power consumption for the manufacture of 1 ton of cathode zinc can be calculated from the equation common to all electrolysis variants. In accordance with the Faraday law, deposition of 1 ton of cathode zinc requires a power consumption of

$$W = \frac{10^6 \cdot 2 \cdot 26.8}{65.38} \cdot \frac{v}{K_e} = 0.818 \cdot 10^6 \frac{v}{K_e} \text{ Wh/t*},$$

$$W = 0.818 \cdot 10^3 \frac{v}{K_e} \text{ kWh/t}$$

where: W = power consumption, kWh/t
v = voltage across cell, V
K_e = current efficiency, %

The voltage across the cell includes the electrode potentials and voltage drops in the cell circuit (33).

The IR value is most affected by current intensity and resistance of the electrolyte. An increase in current density raises oxygen overvoltage at the anode, and, therefore, both the E_a and v values.

Voltage across the electrolysis cell can be reduced by bringing the electrodes closer together, raising the temperature and the sulphuric acid content in the electrolyte. However, too close an arrangement of electrodes carries a risk of short circuit.

Factors that determine current efficiency have been discussed above. Their action opposes that of factors necessary to reduce cell voltage in that they involve greater current density and lesser both temperature and acidity of the electrolyte.

A complete deposition of zinc is disadvantageous because of a sharp drop in current efficiency toward the end of electrolysis.

After the plating of a portion of zinc, generally 80 to 100 kg per 1 m^3 of electrolyte, and the accumulation of an equivalent amount of free sulphuric acid, the electrolyte is withdrawn from the electrolysis tanks and used for lea-

* If the out-of-system unit of electric power kilowatt-hour (kWh) is expressed in units of the SI system (joules, j), we obtain: 1 kWh = $= 10^3$ W·3600 s = $3.6 \cdot 10^6$ W·s = $3.6 \cdot 10^6$ j = 3.6 Mj.

But, in order not to complicate the text, we conduct the calculation in kilowatthours.

ching the roasted concentrate. Zinc remaining in the electrolyte is not lost, as it is recycled. Therefore, it is good practice to conduct electrolysis in a manner to deposit a maximum of zinc compatible with optimum both electrolyte acidity and current efficiency.

Power consumption is at its least when electrolysis conditions are optimum.

Acidity, for example, is a function of current density, as:

Current density, A/m^2	300-450	600-700	900-1000
Acidity, gram/litre	90-110	150-170	280-300

Too high an acidity, an operating risk because of a rapid corrosion of the equipment, requires intensive both circulation and cooling of the electrolyte.

Most of the plants operate according to the former two modes, leaving 40-60 gram/litre of zinc in spent electrolyte. Hence, a neutral solution then contains 100 to 150 gram/litre of zinc.

Stirring of the electrolyte to homogenize its composition and prevent concentration polarization is attained by circulation, i.e., by appropriate feeding and discharge of the electrolyte. A customary circulation of 3-5 litre/min can be raised somewhat, if a portion of spent electrolyte is supplied to the tanks.

Ions of impurities listed in Table 25 are stronger oxidizers than Zn^{2+} and should settle out at the cathode before zinc. However, their concentrations (activities) in the electrolyte have been lowered by preliminary purification. Cathodes may be contaminated by these metals at excessive current loads, when too high a current density and insufficient stirring result in a concentration polarization. The higher the current density, the purer should be the electrolyte.

Contaminating copper, nickel and cobalt that settle at the cathode together with zinc, form an alloy whose hydrogen overvoltage is lower than that of zinc. Subsequently, this area becomes the site of predominant evolution of hydrogen, which causes a drop in zinc current efficiency. Besides, pores and through holes that tend to appear on the cathode deposit, increase its surface area and thus lower current density and consequently, the current efficiency.

Iron does not contaminate the zinc deposit but affects adversely current efficiency. Ferrous oxide reduces to ferric oxide at the cathode, while at the anode, ferric oxide is re-oxidized. Oxidation and reduction of iron circulating in the electrolyte consumes an additional amount of current.

Cadmium and lead have almost no effect on the current efficiency, but contaminate the cathode deposit. Presence of lead ions in the electrolyte is due to the accumulation of chlorine ions which enhance corrosion of electrodes.

If colloid surfactants are added to the electrolyte, the effect is greater hydrogen overvoltage and less unfavourable action of some of the impurities. A standard practice is to add joiner's glue to the electrolyte in amounts of 200-400 gram/ton of zinc. The use of surfactants does not eliminate the need for purification of the liquor prior to electrolysis.

The structure of the cathode deposit has a decisive effect upon both the electrolysis and the subsequent melting of cathodes. Irregular, porous, loose or punctured deposits present greater surface area than the solid and the smoother ones, and, what is more, poor quality of deposits decreases current density and, in its turn, lowers both hydrogen overvoltage and current efficiency. Electrolytic zinc that plates out at the cathode tends to form tree-like crystals (dendrites) which grow at right angle to the surface of the cathode in the direction toward the anode and may be the cause of short-circuits.

Cathode deposits are greatly improved by the introduction of surfactants. The result is more uniform and dense deposits with smoother surfaces.

The action of surfactants is explained by their sorption on areas of a maximum surface energy, e.g., on sharp edges of irregularly oriented crystals. Further deposition of zinc slows down at points of sorption.

Electrolytic Tank Design

The tanks are built of concrete, wood or steel and protected against attack by electrolyte by lead, acid-resistant brick or sheet vinyl plastic. On the outside, they are coated with varnishes, bitumens or sheet vinyl plastic to ensure

greater service life. Wooden tanks are cheaper than concrete ones, but their durability is lower.

Tanks are placed on concrete piers up to 6 m high on insulating liners from glass or porcelain and connected in nests of 20-25 units that adjoin on each other by their longer walls (Fig. 81).

Anodes are cast of lead alloy with 1% Ag, which may contain some thallium, cobalt, arsenic and other metals

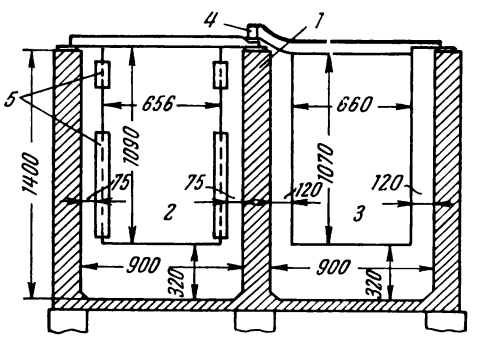

Fig. 81. Section through adjacent electrolytic cells illustrating layout of electrodes

1—common longitudinal wall; *2*—anode; *3*—cathode; *4*—anode-to-cathode contact; *5*—limiting strips from vinyl plastic

that tend to slow down anode corrosion. To increase surface area and thus decrease anode current density and to improve electrolyte circulation, anodes are made either in perforated or wafer design and thicknesses of 6 to 8 mm.

A lead-plated copper bar is welded to the top edge of an anode, while side edges of anodes are fitted with vinyl plastic strips that prevent short-circuits inside tanks.

Cathodes are cut of rolled or ground aluminium, their length and width being by 20-25 mm greater than that of anodes. To facilitate stripping of zinc, edges of cathodes are clad with rubber or vinyl plastic U-shaped planks. Aluminium bars with copper contacts at one of the arms are welded to the top edge of cathode.

Each tank takes 28-30 cathodes and by an odd anode more. Both the cathodes and the anodes alternate at distances of 28-35 mm one from another and rest on tank edges

by ends of bars. Ends of cathode bars are placed upon anode bars of a preceding tank (see Fig. 80) and so ensure a series circuit. Voltage across tank ranges from 3.5 to 3.7 V, depending on electrolyte acidity and electrode spacing. If this value is multiplied by the number of the series tanks, the product is the voltage required for supplying the series with power. The voltage should correspond to ratings of the current converter available, account taken of voltage drops in connecting circuits and busbars.

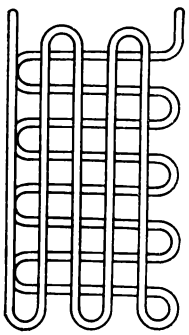

Fig. 82. Aluminium coiled pipe for cooling electrolyte

At zinc electrolytic plants, generally used are mercury rectifiers as at the relatively high voltages that are required they provide a greater efficiency than generator motors. Current intensity in tank circuit is commonly 10 000 to 150 000 A, and the voltage, 500-650 V. There are electrolytic zinc plants which are supplied with power from silicon rectifiers that are even more economical.

A neutral liquor, cleaned of impurities, is fed from a pressure tank via piping or vinyl plastic troughs to each of the electrolytic tanks by means of a rubber hose with an adjusting clip. Spent electrolyte flows out at the opposite end through a discharge pocket and launder to a collector whence it is withdrawn to leaching.

To ensure high current efficiencies, the electrolyte temperature should be kept below 30-35°C, but practically it attains 45°C. Taking into account heating by the current, the electrolyte is cooled before it enters tanks or inside the tanks. This is achieved by flat coiled pipes of aluminium placed at front edges of tanks near the electrolyte inlet (Fig. 82). Coiled pipes occupy vital tank space, and, therefore, it is good practice to cool the electrolyte before it is supplied to tanks. Of the many suggested devices, one that seems to offer greater prospects is a vacuum-vaporizer which has been introduced industrially by a limited number of plants. The principle of extracting the latent heat of vaporization of the electrolyte as it boils under vacuum conditions underlies the performance of the vacuum vaporizers.

Electrolysis Practice

Operation of an electrolysis plant involves supervision of tanks, grinding and placing of cathodes, stripping zinc off cathodes, replacement of anodes and cleaning tanks of anode mud.

Supervision of tank operation includes measurement of voltages across electrodes and of electrolyte temperature, determination of the composition of spent electrolyte and adjustment of its circulation. An increase in voltage is indicative of poor electrical contact, and the trouble should be remedied too on the spot. A sharp drop in or absence of voltage across a tank indicates a short-circuit which should be immediately eliminated.

Cathode zinc is stripped off once every day, the operation being performed by withdrawing 5-7 cathodes at a time. Stripping of the cathodic deposit, which generally offers no problem, is performed manually and may be facilitated by introducing a small amount of antimony compounds.

Stripped zinc is transferred to melting department, while cleaned cathodic sheets are placed back into tanks, sheet surface being, whenever necessary, scraped clean with steel brushes. Anode life is one and a half to two years.

Anode mud consists of manganese salts, and of lead compounds, the contents being about 70% MnO_2, 10-14% Pb, up to 2% Zn. Anode mud, used for oxidation of iron in neutral leaching, should be removed off anodes at regular intervals, as its build-up tends to raise the electrical resistance between the anode and the electrolyte.

Oxygen bubbling off the anodes entrains minute electrolyte droplets with the effect that an acid mist appears in plant atmosphere. The mist is injurious to health of operators as it may irritate skin and higher respiratory tracts and cause tooth decay. Plant equipment and roofs of buildings also tend to corrode when attacked by the acid mist.

To avoid splashing, a strong froth is built on the surface of the electrolyte by additions of frothing agents, such as soap root extract.

Melting of Cathodes

Stripped cathodic zinc sheets are washed then melted in low-frequency (commercial frequency) induction furnaces at a temperature of about 500°C. Zinc tends to oxidize in molten state, and the resultant oxide film separates zinc droplets and prevents their coalescence, melt surface then becoming covered with an accumulation of loose scale, or dross.

Formation of dross may be minimized by addition of ammonium chloride which dissociates to ammonia and hydrogen chloride as it volatilizes. The latter interacts with zinc oxide to give molten zinc chloride (melting point 318°C) of a high surface tension. Denudation of zinc droplets promotes their coalescence.

A small amount of zinc vapours is carried away by outgoing gases and collected from them in the form of oxide. Zinc lost with dross and dust totals about 2.5%.

Molten zinc is cast into moulds in casting machines, its purity being 99.97-99.99%, which corresponds to grades Ц1 and Ц0 as specified by the USSR State Standard GOST 3640-65.

For a practical current efficiency of 89 to 94%, power consumption for the electrolysis of one ton of zinc lies between 11 160 and 11 880 Mj (3100 to 3300 kWh), while its overall consumption per ton of pig metal is 14 400 Mj (4000 kWh).

42. Manufacture of Cadmium

Cadmium, similarly to cobalt, is referred to minor metals. Practically, it has no individual ores and is recovered from zinc concentrates as a side product. Relatively lesser amounts of cadmium are extracted from blue powder and sublimates of lead manufacture and from storage battery scrap, but in this case as well the operation is performed at zinc smelters where cadmium plants are generally built.

Cadmium is remarkable for its capacity to capture thermal neutrons, and this has predetermined its use for the manufacture of rods that control atomic reactor operation.

Cadmium is also required for the manufacture of alkali storage batteries. Some amounts of cadmium are consumed

for ornamental and anticorrosive coatings, for the manufacture of antifriction alloys and in dentistry. Small additions of cadmium have little effect upon electrical conductivity, but appreciably raise mechanical strength of copper. Cadmium bronzes are used for the manufacture of trolley and other types of suspension conductors.

Cadmium serves as a base metal for bearing alloys intended for heavy duty in aircraft, automotive and ship-borne prime movers. Cadmium is also a component of babbitts. Of great interest are alloys of cadmium with bismuth, lead, tin and zinc whose melting points range from 21.5 to 164°C. Low-melting alloys are used to join glass with metal, in automatic fire extinguishers, sprinklers, and for the manufacture of precise anatomic patterns.

Cadmium oxide CdO is brown in colour. It is used as a catalyst for hydrogenation of fats and component of luminous compounds.

Cadmium sulphide CdS serves as a colour for art painting (cadmium yellow) and as an addition for the manufacture of colour glass.

Raw Materials for Cadmium Production

Minerals Greenockite CdS, and such minerals as $CdCO_3$ "otavite" and CdO "monteponite" are rare. Cadmium ores as such are unknown. Cadmium enters the composition of polymetallic ores as a solid solution in sphalerite and other sulphides. In selective flotation cadmium distributes itself between lead and zinc concentrates. In sintering of lead and zinc concentrates, cadmium goes off with fumes and is collected as dust. In roasting zinc concentrates for hydrometallurgical processing, the concentration of cadmium in dust is not high as temperatures involved are relatively low.

Boiling (or sublimation) points of Cd, CdO and CdS are 765, 1560 and 1380°C respectively. Therefore, the metal and the sulphide are more volatile than oxide. At temperatures of about 1000°C the reaction

$$2Cd\,) + CdS \rightarrow 3Cd + SO_2$$

proceeds at an intensive rate and explains the chief mechanism of cadmium volatilization in roasting.

In leaching of roasted concentrates, some 80-90% of cadmium goes in solution from which it is recovered into a copper-cadmium cake. In waelzing of zinc cakes, cadmium goes to fumes.

Pyrometallurgical processing of zinc concentrates transfers a portion of cadmium to dust that is collected in roasting, while in distillation cadmium passes to crude zinc and, to a lesser degree, to blue powder. However, blue powder is higher in cadmium.

Raw materials for the production of cadmium is dust collected in sintering of lead and zinc concentrates, blue powder, fumes, copper-cadmium cakes and other waste of lead and zinc production, among them storage battery scrap.

Cadmium production technique is quite complicated, and, therefore, the metal is extracted in specialized production shops of zinc electrolytic plants.

To minimize transportation coats, cadmium waste is given primary concentration where it is obtained. To this end, dust, sublimates and blue powder are leached with sulphuric acid. Lead sulphate, silicic acid and other insoluble impurities remain in the residue, while zinc and cadmium pass in solution as sulphates. From the liquor, cadmium is extracted by cementation with zinc dust, and the resultant cadmium sponge is subsequently processed in cadmium production shops.

A flowsheet for manufacturing cadmium from a copper-cadmium cake or sponge is given in Fig. 83.

The cake is leached with spent electrolyte of zinc manufacture, more specifically, by the sulphuric acid the electrolyte contains, leaching involving heating to 80-90°C and air agitation. The air also serves as an oxidizer which speeds up solution. Sometimes, MnO_2 is added for the same purpose. Zinc, cadmium and contaminating nickel, cobalt and copper dissolve in the order as listed, which order correlates with oxidation-reduction potential values (see Table 3). In a general form, the solution may be described by the schematic reaction (36), while resultant ions Cu^{2+} are substituted in a cementation process by other sponge components, as,

$$Cu^{2+} + Cd \rightarrow Cu^{\circ} + Cd^{2+}$$

The liquor obtained is cleaned of copper, cementing by zinc dust, while cadmium sponge is settled out by the same zinc dust once cement copper has been precipitated.

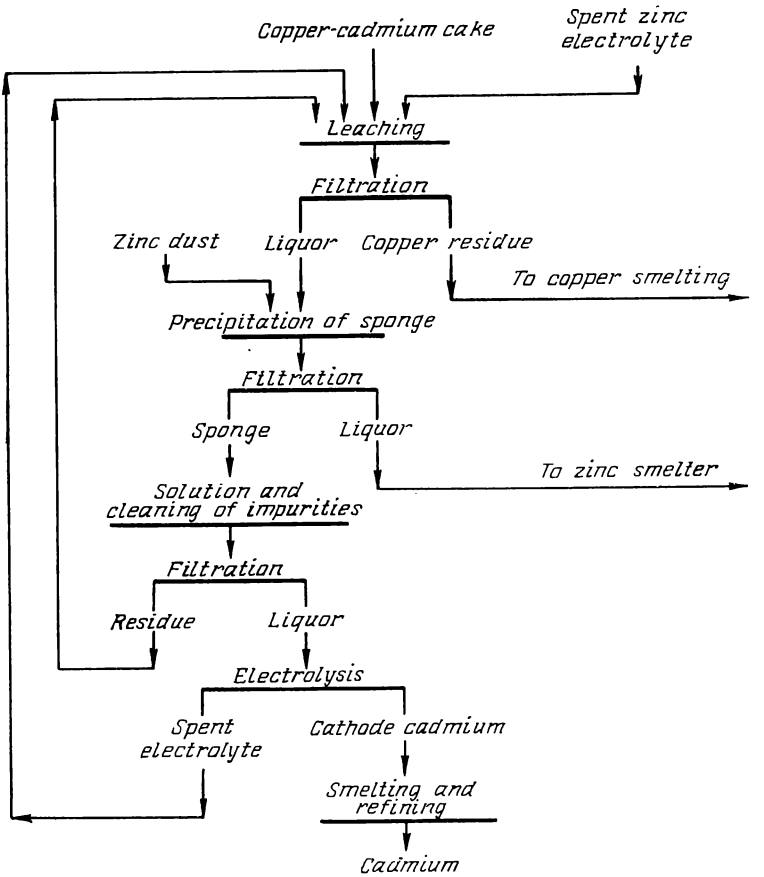

Fig. 83. Flowsheet for production of cadmium from copper-cadmium cakes

Primary cadmium sponge, bought out or obtained from copper-cadmium cakes, is dissolved in sulphuric acid. Liquors are thoroughly cleaned of iron, arsenic, antimony,

copper and other impurities and transferred to electrolysis. Cathodic cadmium is melted under an alkali blanket to avoid its oxidation and to clean it additionally of zinc. When a sponge low in cadmium is involved, the solution in sulphuric acid and cementation of cadmium by zinc is repeated a number of times.

Besides cadmium, zinc concentrates may yield such by-products as indium, thallium and sometimes germanium.

Review Questions

1. Name chief consumers of zinc.

Manufacture of alloys and galvanic cells, zinc-plating of iron, manufacture of zinc white.

2. What metals pass chiefly to zinc concentrates in ore dressing?

Au, Ag, Bi, Cd.

3. What impurities are separated from zinc in leaching of roasted concentrates?

Cd, Co, Cl, Fe, As, Sb, Si, Cu, Pb.

4. What impurities in an electrolyte affect adversely physical properties of zinc deposit?

Fe, Cu, Co, Cl, Cd, Pb.

5. What governs current efficiency in electrolysis of zinc?

Voltage across electrolytic tank, temperature, current density, circulation of electrolyte, tank size, acidity of electrolyte, zinc content in electrolyte, purification of electrolyte.

6. What impurity in zinc concentrates is the chief factor affecting zinc recovery?

SiO_2, Cu, Fe, Cd, S.

7. What metals are recovered from zinc hydrometallurgy waste, the zinc and the copper-zinc cakes?

Cu, Fe, Cd, Bi, Ti, Pb, Au, Ag.

PART II

METALLURGY OF LIGHT METALS

CHAPTER 6

GENERAL

A group of light metals, related to aluminium, that has rendered possible many an engineering breakthrough since the beginning of this century, is today used in ever increasing quantities for a variety of industrial and household applications.

This group of industrial classification, based on a density below 5, includes aluminium, magnesium, titanium, beryllium, calcium, barium, strontium, lithium, potassium, sodium, rubidium and cesium. Today all the light metals without exception are essential to various branches of engineering, but the major ones among them are aluminium, magnesium and titanium. These three metals are used in pure state and in alloys, where they are the base metals.

Other light metals are unsuitable as structural materials, as they lack in requisite properties, and, to top it all, are costly. They serve, however, as additives to different alloys or are used as chemical compounds.

Discussed below are the chief engineering properties of aluminium, magnesium and titanium.

Aluminium

Aluminium has a low density, and it is almost three times lighter than iron. Pure aluminium is very soft, but, if alloyed with small additions of other elements, its mechanical strength increases many times, with increasing its density, but negligibly. A feature of aluminium alloys is a combination of strength, lightness and corrosion resistance.

Substitution of iron and copper by aluminium or its alloying greatly reduces the weight of structures and mechanisms. In the first quarter of this century, this has happened to be of a crucial importance for aeronautics which was then making its first steps and has served a rapid development of aircraft engine building. Besides, aluminium has made possible the manufacture of lightweight automotive engines, railroad rolling stock and other means of transport, and this, in its turn, has favoured greater transportation speeds and better safety owing to easier braking.

As a material for internal combustion engines, aluminium's major advantage is its high heat conductivity.

Today the use of aluminium as a structural material becomes more and more diversified. In recent years, aluminium finds extensive application in the manufacture of building components, such as window and door frames, handrails, roofing and slabs for erecting buildings.

Aluminium alloys containing an aggregate of not more than 10% of copper, manganese, magnesium and zinc are comparable in strength and hardness with steel, while their density often exceeds 3000 kg/m^3.

Alloys of this kind are amenable to mechanical working, and they can readily be worked by rolling, forging, die forging, rolling and machining.

Foundry aluminium alloys are of a great convenience as regards founding practice, as they readily reproduce mould configuration owing to silicon additions. These alloys are also lightweight and adequately strong. Cylinders, pistons and other parts of aircraft and automotive engines are cast from these types of alloys.

Pure aluminium often replaces copper in electrical engineering, being used in the manufacture of conductors, busbars, contacts and other articles that are required to have a high electrical conductivity. Although the latter is 65% only of that of copper, the density of aluminium is almost three times as less, which means a lesser consumption of metal. Suspension of aluminium conductors calls for fewer poles than that of copper conductors.

Simplicity of mechanical working, excellent appearance of articles and their lightness have been decisive factors in promoting the use of pure aluminium and of some of its

alloys in instrument building and in the manufacture of housings of cinema equipment and photo cameras, measuring instruments, radio receivers and other similar articles.

The surface of aluminium and of its alloys is always coated by a thin but strong layer of oxide Al_2O_3 which protects it against further oxidation and allows it to retain a good appearance for a long time. If the surface film is scratched or damaged in any other way, it reconstitutes itself so forth under the action of air oxygen. The film is extra strong if it is obtained by electrolytic oxidation (anodizing). The film can readily be painted in any colour, and this is widely taken advantage of in jewellery and in clock and watch manufacture.

The strength of the surface film and its harmlessness to users make aluminium suitable for the manufacture of various equipment in the chemical and the foodstuff industries, as, the manufacture of utensils, foil and packages for foodstuffs.

Along with the advantages of the surface film, a shortcoming inherent in it should not be overlooked: the film makes difficult the soldering and the welding of aluminium, which can be carried out through the agency of special techniques only.

Metallic aluminium powder goes for the manufacture of silver paint, which is both ornamental and strong and possesses anticorrosive properties. The paint is prepared by mixing aluminium powder with drying oil or other vehicles.

In quantity, aluminium raw materials greatly surpass the natural resources of other nonferrous metals, and today aluminium smelting costs are on a downward trend. All this concurs to single out aluminium as a metal of the future, one which can potentially replace not only heavy nonferrous metals, but iron as well.

Magnesium

Magnesium is even lighter than aluminium, but it poorly resists the action of atmospheric air, particularly one laden with water vapours. Therefore, pure magnesium is of no use as a structural material.

Alloys of magnesium with aluminium, zinc, manganese and some other metals are adequately corrosion resistant. These alloys, readily castable and machinable, have found a wide application in the manufacture of aircraft and automotive prime movers and in rocketry. Of a great interest are alloys of magnesium with lanthanides which retain a high mechanical strength at temperatures up to 300°C.

Structures from magnesium alloys are by 25% lighter than those from aluminium, while the cost of a unit volume of structures is almost as lower; this makes the use of magnesium alloys very advantageous in machine building.

A high affinity of magnesium for oxygen allows its use as a reducer for metallothermic reactions.

Titanium tetrachloride and uranium fluoride are reduced to metals by magnesium. Present-day titanium manufacture consumes a great proportion of magnesium output.

The high affinity of magnesium for oxygen and its ability to burn in the air with an evolution of large quantities of heat and light is put to use in military engineering in the manufacture of incendiary shells and flares.

Titanium

Titanium has become an industrial material relatively recently. In the second quarter of this century only, it became possible to obtain it in a sufficiently pure state, and this has been rewarded by the discovery of new valuable properties, such as forgeability and amenability to mechanical working.

Titanium is somewhat heavier than magnesium and aluminium, but it is stronger and very resistant to corrosion. Particularly strong are alloys of titanium with aluminium, manganese, chromium, iron and some rare metals. In strength, they are not inferior to steel, but, by contrast, are almost twice as lighter. In corrosion resistance, titanium surpasses stainless and acid-resistant steels.

As regards general purpose structures, titanium is as yet quite costly, but it has become indispensable in some industrial applications. Heat resistance of titanium and of its alloys extends to temperatures of 400-450°C, whereas aluminium and magnesium alloys tend to fail even at as low

temperatures as 200-300°C. This is why as jet aircraft developed, titanium alloys became their basic materials. The temperature of the body of a jet aircraft in flight rises to 300°C, and in prime movers it is even higher. Titanium alloys are used for the manufacture of engines and fuselages of jet aircraft, of rockets and shells of artificial earth satellites.

Use of titanium in military engineering reduces the mass of tanks and guns, and so enhances their speed and manoeuverability.

In shipbuilding, in atom-powered ships in particular, titanium and its alloys are bound to find a wide use as heat resistant materials of a high corrosion resistance.

Review Questions

1. Arrange light metals in the order of increasing melting points, electric conductivities and corrosion resistances.

Al, Mg, Ti.

2. Name chief components of alloys based on aluminium and titanium.

Mg, Fe, Cu, Si, Al.

CHAPTER 7

METALLURGY OF ALUMINIUM

43. Chemical Properties of Aluminium

Aluminium is an element of group III of the D. I. Mendeleev's periodic table. On the outer shell, it carries three electrons which it gives off when exhibiting its highest valency of three. There are also monovalent and divalent aluminium compounds, but they are not stable.

Aluminium is less active than sodium and magnesium, this following from its place in the voltage series (Table 3). Despite a great negative potential, aluminium fails to decompose water and is fairly stable against the action of diluted acids owing to the tightness of the oxide film. The latter slowly dissolves in diluted or concentrated acids, nitric and sulphuric ones and can be attacked to a greater extent by the same acids, if the latter are diluted to medium concentrations, and by chlorhydric acid. Once the surface film is damaged, the metal dissolves rapidly. For example, in a chlorhydric acid, the reaction is

$$2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2 \qquad (174)$$

Alkalis dissolve the surface film to give an aluminic acid salt, sodium aluminate

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O \qquad (175)$$

after which aluminium reacts with water:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \qquad (176)$$

Resultant aluminium hydroxide also gives an aluminate

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O \qquad (177)$$

It is more correct to represent reaction (177) as one involving hydration and formation of complex anions

$$Al(OH)_3 + OH^- \rightleftarrows [Al(OH)_4]^-$$

$$Al(OH)_3 + 3OH^- \rightleftarrows [Al(OH)_6]^{3-}$$

The latter in an empiric form are respectively equivalent to $AlO_2^- \cdot 2H_2O$ or $AlO_3^{3-} \cdot 3H_2O$, or simply as AlO_2^- and AlO_3^{3-}.

The ability of aluminium to react with acids as well as with alkalis is due to the amphoteric character of its oxide which can exhibit either acid or alkaline properties. In an acid medium, aluminium hydroxide, similarly to bases, dissociates to ions

$$Al(OH)_3 \rightleftarrows Al^{3+} + 3OH^-; \quad pK = 32.0 \qquad (178)$$

while in alkaline media it dissociates similarly to acids

$$H_3AlO_3 \rightleftarrows H^+ + AlO_2^- + H_2O; \quad pK = 12.80 \qquad (179)$$

Reactions (178) and (179) allow ready calculation of the range of pH where $Al(OH)_3$ fails to dissolve by assuming that activities of Al^{3+} or of AlO_2^- are less than or equal to 10^{-5} gram-ion/litre.

From (178), we obtain

$$K = a_{Al^{3+}} \cdot a_{OH^-}^3 = 10^{-32}$$

$$P_{OH} = \frac{32-5}{3} = 9; \quad pH = 5$$

From (179), we find

$$K = a_{H^+} \cdot a_{AlO_2^-} = 1.6 \cdot 10^{-13}; \quad pK = 12.8$$

$$pH = 12.8 - 5 = 7.8$$

Mechanical strength of the oxide film and its immediate renewal after damage are explained by a high affinity of aluminium for oxygen and a high rate of oxidation.

The ability of aluminium powder to vigorously oxidize in the air while developing temperatures of up to 3000°C is also due to its high affinity for oxygen. Oxidation of aluminium is also possible at the expense of oxygen that is chemically bound in oxides of other metals, as,

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$

A mixture of aluminium powder with iron oxide, or thermit, was formerly used on a wide scale to weld together iron parts, e.g., rails at joints. Similar reactions with other oxides are suitable for reduction of refractory metals such as manganese, chromium, tungsten and others, the method being termed aluminothermics.

Owing to a high affinity for oxygen, aluminium can be reduced from its oxide by carbon at temperatures of about 2500°C only, the resultant being a mixture of metal and carbide

$$2Al_2O_3 + 6C = 4Al + 6CO \quad (180)$$

$$4Al + 3C = Al_4C_3 \quad (181)$$

However, a reduction smelting is unsuitable for the production of aluminium owing to a vigorous volatilization of monovalent and divalent aluminium oxides.

Aluminium oxide Al_2O_3 is a white fine crystalline substance having density of 3960 kg/m^3, melting point of 2050°C and boiling point of 2980°C.

Natural forms of Al_2O_3 are described below, while it may be produced artificially by burning aluminium in the air or calcinating the hydroxide $Al(OH)_3$.

High melting point of Al_2O_3 explains its use as a refractory material (corundum). A high hardness of corundum makes it suitable for the manufacture of grinding stones and as a grinding (abrasive) powder.

When acids act upon an aluminate liquor, aluminium hydroxide precipitates as a result of hydrolysis: the acid neutralizes the excess of hydroxyl ions, after which the aluminate hydrolizes with the formation of $Al(OH)_3$. For example, when gaseous carbon dioxide reacts with an alkali sodium aluminate liquor, the following reactions take place

$$2NaAlO_2 + 4H_2O \rightleftarrows 2Al(OH)_3 + 2NaOH$$

$$2NaOH + CO_2 \rightleftarrows Na_2CO_3 + H_2O$$

$$2NaAlO_2 + CO_2 + 3H_2O \rightleftarrows 2Al(OH)_3 + Na_2CO_3 \quad (182)$$

In calcination, aluminium hydroxide loses water and turns to Al_2O_3

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \quad (183)$$

Depending on calcination temperature, resultant Al_2O_3 is either a loose hygroscopic γ-Al_2O_3 (800°C) or a more dense α-Al_2O_3 (1200°C), but generally the product is a mixture of both components due to a flow rate of transformation.

Aluminium has a low affinity for sulphur, and, therefore, no sulphides occur naturally. A sulphide obtained artificially decomposes rapidly from the action of atmospheric moisture

$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S \qquad (184)$$

44. Ores for Production of Aluminium

Aluminium is found in such ores as oxide minerals, more specifically, oxides, double basic sulphates and silicates. As the separation of aluminium from a chemically similar silicon is difficult, the former may best be extracted from ores that carry hydrated aluminium oxide in the form of minerals hydrargillite, boehmite and diaspore (Table 26).

Table 26

Major Minerals of Aluminium

Name of mineral	Formula	Content of Al_2O_3, %
Corundum	Al_2O_3	100
Diaspore, boehmite	$Al_2O_3 \cdot H_2O$	85
Gibbsite (hydrargillite)	$Al_2O_3 \cdot 3H_2O$	65.4
Nepheline	$(Na_xK_y)O \cdot Al_2O_3 \cdot 2SiO_2$	32-36
Alunite	$(Na_xK_y)SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$	37-39
Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	39.5
Kyanite (andalusite, sillimanite)	$Al_2O_3 \cdot nSiO_2$	63.2

A chief source of aluminium are bauxite ores which contain hydrargillite, boehmite or diaspore and, sometimes carry small amounts of corundum and alumosilicates, and always, some titanium, vanadium, chromium, gallium, while barren rock contains hydrated iron oxides, various

aqueous silicates and calcium and magnesium carbonates. The chemical composition of bauxites from some of USSR deposits is listed in Table 27.

Table 27

Average Chemical Composition of Some Deposits

Type of bauxite	Content, %			
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2
Boehmite-diaspore	51-57	2.5-8.5	20-22	2.5-3
Same	48-60	5-12	18-20	2.5-3
Hydrargillite	33-39	6-8	15-20	3-4
Same	32-46	6-10	25-35	4.8-5.5
Hydrargillite-boehmite	39-46	8-15	14-16	2-3

Quality of bauxites is evaluated in terms of Al_2O_3 content and its mineralogical form, hydrargillite bauxites being preferred. Besides, account is taken of the silicon module, or the ratio of Al_2O_3 and SiO_2 percentages which should be as high as possible.

In addition to the production of aluminium, bauxites also serve as a starting material for the manufacture of electrocorundum, aluminous cement, refractory articles and as flux and refractory powder in open hearth steelmaking.

Nepheline-Bearing Rock

Quality of these ores is evaluated in terms of the Na_2O: Al_2O_3 ratio which should be as close as possible to unity and in terms of a minimum iron content. Nepheline sometimes occurs together with apatite $(Ca_{10}G_2(PO_4)_6$, where G is fluorine or chlorine. Apatite is separated by flotation and used in fertilizer production, whereas recleaned tailings yield a nephelite concentrate of a following approximate composition: 30% Al_2O_3, 20% $Na_2O + K_2O$, 44% SiO_2.

Nephelite syenites carry less nepheline and no apatite, and, to top it all, are contaminated by iron to a greater extent. After removal of a proportion of iron by magnetic separation, nepheline-syenite concentrates are processed to alumina and side products, soda and cement.

Alunites, Clays, Kaolins and High-Alumina Silicates

Rock containing isomorphic mixtures of sodium and potassium alunites may be valuable raw materials for the production of alumina, K_2SO_4, soda and sulphuric acid.

Clays carry kaolinite, and, if a clay contains not less than 30-32% Al_2O_3, it may serve as a low-grade raw material for production of aluminium.

Known as high-alumina silicates are ores that carry a large amount of andalusite, sillimanite and kyanite and are suitable for direct smelting of aluminium and silicon alloys, or silumins.

45. Aluminium Production Techniques

Difficulties involved in the reduction of Al_2O_3 by carbon have for a long time delayed the development of aluminium production.

Aluminium was obtained for the first time by a Danish chemist Oerstedt in 1825 by the action of potassium amalgam upon $AlCl_3$. This technique was then improved by Weller, and a small scale manufacture of aluminium was started in France in 1854. The production technique was far from perfect, resultant metal was of a poor quality, costly and found no wide demand. In 35 years of operation, the plant's output was only 35 tons of aluminium.

In 1886, both Ch. Hall in USA and P. Héroult in France have suggested to obtain aluminium by electrolysis of alumina dissolved in molten cryolite Na_3AlF_6. To date, this method is still a most convenient and advantageous one, and is in use at up-to-date plants.

Fig. 84 shows a schematic diagram of an aluminium reduction cell. Its bottom and walls are lined with carbon blocks and carbon slabs baked from fine petroleum and pitch cokes.

The cell is filled with molten cryolite, which carries in solution up to 8% of alumina. A carbon electrode dips into

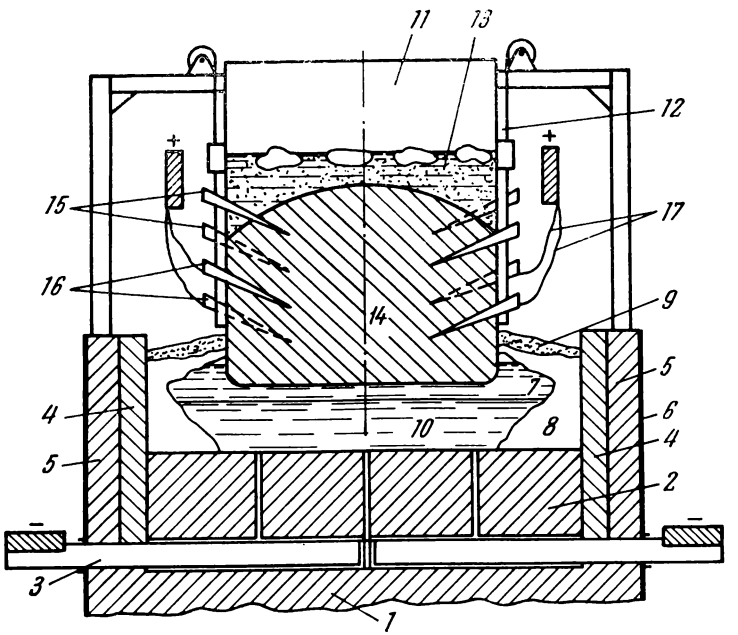

Fig. 84. Alumina electrolysis cell

1—foundation; *2*—carbon lining; *3*—busbar supplying current to hearth; *4*—carbon slabs; *5*—fireclay brickwork; *6*—steel shell; *7*—molten electrolyte; *8*—solid crust of electrolyte; *9*—alumina prepared for charging; *10*—molten aluminium; *11*—anode; *12*—anode aluminium shell; *13*—anode paste; *14*—conical baked portion of anode; *15*—rods for securing anode to suspension device; *16*—rods for supplying electric current; *17*—flexible busbars

the melt. Molten aluminium collects on the bottom, as its density, 2340 kg/m^3, is higher than that of the electrolyte, about 2030 kg/m^3 (18).

Oxygen oxidizes the anode to give CO and CO_2. The voltage required for the electrolysis at 950°C is from 1.6 to

1.7 V, that for Fe_2O_3 and SiO_2 impurities being 0.89 and 1.64 V, respectively. The upshot of this is that manufacture of high-grade aluminium calls for a pure alumina.

Production of pure alumina of ores is the first stage dictated by the aluminium manufacture.

In the Soviet Union alumina suitable for aluminium production is subdivided, according to the State Standard GOST 6912-64, into grades ГА85, ГА8, ГА6, ГА5; the former grade carries not more than 0.2% SiO_2, 0.08% Fe_2O_3, 0.6% (Na_2O + K_2O) and up to 1.2% moisture.

There are different techniques for winning aluminium from various types of ores. A technique for production of Al_2O_3 from bauxites was developed for the first time at the end of the last century by K. I. Bayer, an Austrian who was resident and worked in Russia.

The *Bayer process* is based on the reversibility of the reaction between the hydrated aluminium oxide and an alkali (177).

When bauxite is heated together with a concentrated alkali, aluminium oxide goes in solution as sodium aluminate, the reaction proceeding from left to right. The $NaAlO_2$ liquor is separated from insoluble residue, diluted and cooled this causing hydrolysis of sodium aluminate and throwing down of an aluminium hydroxide deposit.

Hydrargillite reacts with alkali solutions at a temperature of about 100°C. A similar solution of boehmite and diaspore, possible only under a pressure in autoclaves, requires heating to 160-200°C.

Autoclave boiling of ground bauxite with an alkali yields aluminate liquor and an insoluble residue composed chiefly of a reddish brown iron oxide, or red slime. The slime is separated from the liquor by precipitation, filtration and washing after which it is dumped. The aluminate liquor undergoes hydrolysis at continuous stirring. It decomposes with resultant residue. Precipitation is promoted by the introduction into the liquor of a seed, or a previously deposited $Al(OH)_3$. The seed presents ready crystallization centres and thus favours a deposition of relatively large crystals that are amenable to filtration.

Precipitation is carried out over a lengthy period of time (50 to 70 hours) while stirring the solution lightly. A modern

trend is to use air agitation and to implement the process in tanks, termed decomposing tanks. This is why precipitation of $Al(OH)_3$ is termed decomposition.

$Al(OH)_3$ precipitate is separated from the alkali liquor by thickening, filtration and washing, then calcined at 1200°C.

The alkali liquor is concentrated by vaporization, then re-used for the boiling of bauxite. The Bayer process flowsheet is illustrated schematically in Fig. 85.

The Bayer process which was developed toward the end of the last century to meet the needs of Russia's textile industry is today widely used all over the world. It is relatively simple and cheap, but is unsuitable for bauxites high in silica, as the latter reacts with the alkali and passes in solution as sodium silicate

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \qquad (185)$$

Sodium silicate reacts with sodium aluminate to give insoluble alumosilicates, e.g.,

$$2NaAlO_2 + 2Na_2SiO_3 + 4H_2O \rightarrow Na_2Al_2Si_2O_8 \cdot 2H_2O + 4NaOH \qquad (186)$$

This causes a portion of aluminium and alkali to pass to the residue, and the two components are thus lost with red slime.

Bauxites often carry calcium and magnesium carbonates which give soda when treated in an autoclave

$$CaCO_3 + 2NaOH \rightleftarrows Ca(OH)_2 + Na_2CO_3 \qquad (187)$$

$$MgCo_3 + 2NoOH \rightleftarrows Mg(OH)_2 + Na_2CO_3 \qquad (188)$$

Soda may build-up in liquors from the reaction between alkali and atmospheric carbon dioxide. When the liquors are vaporized, soda settles out as monohydrate $Na_2CO_3 \cdot H_2O$ crystals which are separated, then turned to alkali by heating together with lime water

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + \downarrow CaCO_3 \qquad (189)$$

The alkali is recycled.

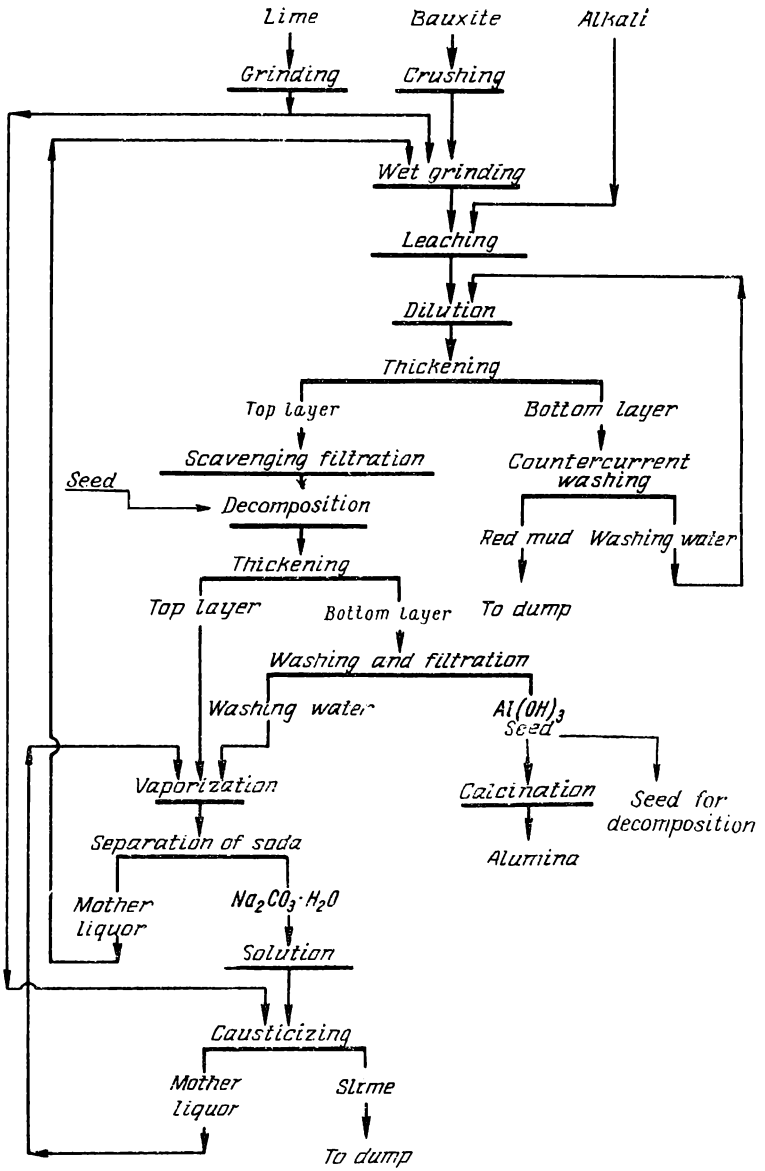

Fig. 85. Manufacture of alumina from bauxites by the Bayer process

Performance calculations tend to indicate that treatment by the Bayer process of bauxites with a silicon module of $\alpha_{si} < 8$ is not always economically advantageous, as much aluminium and alkali are lost with the red slime. For sometime, the aluminium industry has been able to meet all its needs with low-silicon bauxites, but as aluminium consumption increased it had to draw on other raw materials, much higher in silica content.

Fusion (Deville-Pechiney) process. This technique is also based on the transfer of aluminium oxides from bauxite to a water-soluble sodium aluminate, but by the action of soda, which is cheaper, although less active than an alkali, the process then calling for considerably higher temperatures non attainable in water solutions.

Crushed bauxite is fused in combination with soda at 1200°C, sodium aluminate being formed according to the reaction

$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 \qquad (190)$$

Simultaneously, soda and silica produce sodium silicate

$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2 \qquad (191)$$

Besides soda, the charge is blended with limestone or lime. Calcium oxide may also bind itself into aluminate $CaAl_2O_4$ and silicate Ca_2SiO_4, which are insoluble in water.

Owing to a difference in affinity for oxides, soda is consumed chiefly for the formation of sodium aluminate, while lime is bound into a silicate.

The charge composed of bauxite, soda and limestone fuses when heated to 1200°C, and the technique has been named after this production step. The fused mass contains sodium aluminate and insoluble calcium silicate, and only a small amount of SiO_2 forming Na_2SiO_3.

In aqueous leaching, aluminate dissolves, while calcium silicate remains in the insoluble residue. However, some silica passes to solution, which then requires desiliconizing in autoclaves by heating.

Sodium aluminate liquors obtained by fusion are similar to those of the Bayer technique, but they carry some soda instead of excess alkali. In the fusion technique, aluminium

hydroxide can be carbonized by the action of CO_2 to a greater extent, almost to completion, the alkali precipitated in the hydrolysis is bound by the carbon dioxide into soda.

$Al(OH)_3$ precipitate is separated from the solution by thickening, filtration and washing, a calcination at 1200°C turning it to alumina.

Soda liquor is concentrated by vaporization and used for fusing new quantities of bauxite. Of particular convenience is a wet fusion method in which a bauxite-bearing soda liquor is sprayed and fused in a kiln. Wet fusion, suggested and developed in All-Union Aluminium-Magnesium Institute by a team of researchers headed by V.A. Mazel, has simplified the production flowsheet by eliminating the vaporization of large amounts of recycled soda liquors, and replacing dry grinding by wet grinding.

A brief flowsheet of the fusion technique is shown in Fig. 86.

Nepheline processing. Besides aluminium oxide, nephelines contain alkali metals (sodium and potassium), often in amounts sufficient for the formation of sodium aluminate. Potash and soda are obtained as side products from the nephelines.

A nepheline concentrate and limestone having fineness of about 0.1 mm are mixed and fused in rotary kilns by a dry technique at 1300°C. The charge is prepared in accordance with the reaction

$$(Na, K)_2O \cdot Al_2O_3 \cdot 2SiO_2 + 4CaCO_3 \rightarrow$$

$$\rightarrow 2Na(K)AlO_2 + 2Ca_2SiO_4 + 4CO_2 \quad (192)$$

The fused mass is crushed and leached by a hot recycled liquor in agitators. Once separated from slime, the liquor is desiliconized in autoclaves and carbonized. Hydroxide deposit is separated, washed and calcinated. About two thirds of the liquor that remains after the separation of hydroxide is recycled to leaching, while the remaining portion is concentrated by vaporization. Crystallized first is $Na_2CO_3 \cdot H_2O$, then potash K_2CO_3 is settled out by additional vaporization.

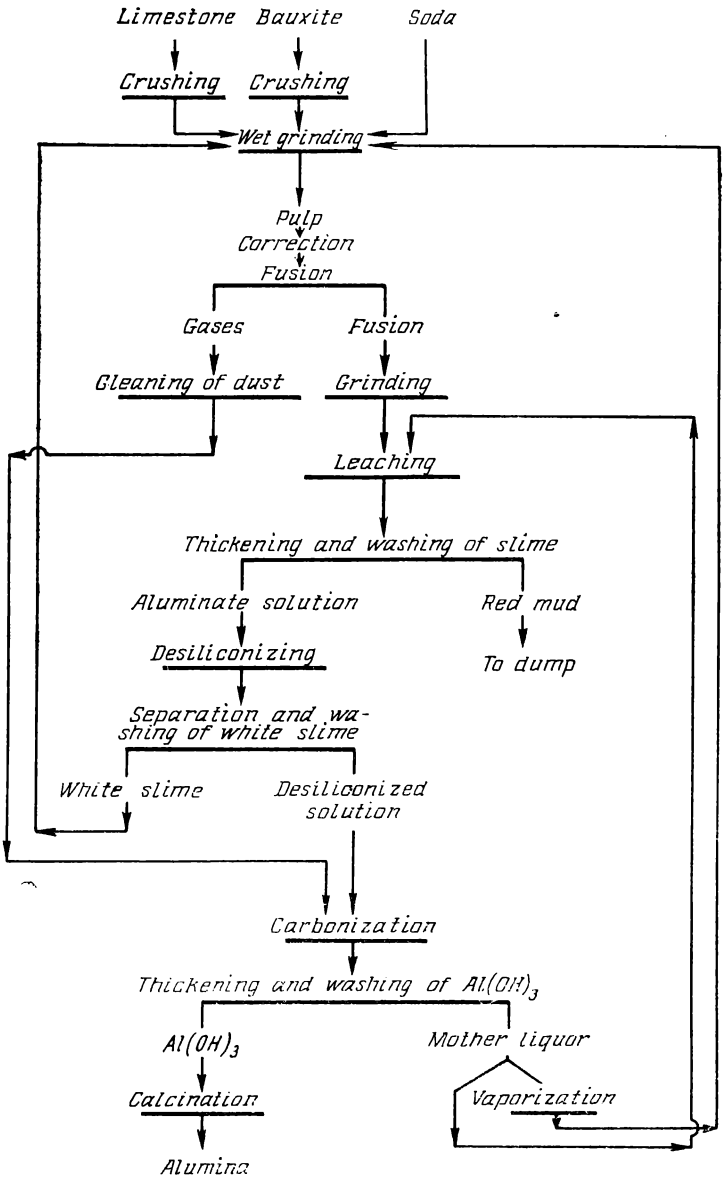

Fig. 86. Manufacture of alumina through fusion

Slime, an insoluble leaching residue, is ground as pulp together with limestone. Its roasting in rotary kilns at 1550°C yields a clinker, whose subsequent grinding to 0.08 mm results in cement.

This complex processing of nepheline allows a side recovery per ton of alumina of about 1 ton of soda and potash and up to 8 tons of cement.

Alumina from the Bayer and the fusion processes, inclusive of that from nephelines, is treated by electrolysis to produce aluminium.

Direct Smelting of Aluminium-Silicon Alloys

In some industries, use is made not of aluminium, but of its alloys with silicon, which are suitable for the manufacture of widely used silumins.

An alloy of silicon with aluminium, silico-aluminium, can be obtained directly from ores, even from ones high in silicon, as kaolins and kyanites.

At a temperature of about 2500°C, aluminium and silicon are reduced to elemental state from oxides by carbon

$$Al_2O_3 + 3CO \rightleftarrows 2Al + 3CO_2$$
$$SiO_2 + 2CO \rightleftarrows Si + 2CO_2$$

Some carbides are obtained parallel with the above products: Al_4C_3(181) and SiC.

The carbides react with remaining oxides to give the alloy

$$2SiC + SiO_2 \rightarrow 3Si(Al) + 2CO$$
$$2Al_4C_3 + 3SiO_2 \rightarrow (8Al + 3Si) + 6CO \qquad (193)$$

Raw materials and the reducing agents are chosen on minimum contents of iron, titanium, sulphur and other impurities.

The reducing agent is a mixture of low-sulphur brown coals with anthracite and either petroleum or pitch coke. The charge is briquetted, sometimes pelletized and smelted in single- or three-electrode arc furnaces of 12-18 MW. Resultant primary alloy contains, %: 50-68 Al; 30-45 Si;

1-3 Fe; up to 2.5 Ti and some non-metallic inclusions. The primary alloy is refined by a number of methods, the simplest of them being smelted under blanket of slag. Silico-aluminium is melted next together with pure aluminium to yield silumins, in which form aluminium is cheaper than its electrolytic grade. The net cost of aluminium is thus reduced by 10 to 35%.

46. Manufacture of Alumina by Bayer Process

Preparation and Leaching of Charge

Bauxite supplied from mines in large lumps is crushed, then ground in ball mills to a size less than 0.06 mm. The liquid grinding medium is generally recycled alkali liquors. Also fed to the ball mill is a fresh alkali to make up for the consumption of the recycled alkali, and lime which speeds up digestion. Grinding also results in an excellent mixing of components.

Aluminium oxide minerals react with alkali liquors at different rates which decrease in the following order: hydrargillite, boehmite, diaspore, corundum. Leaching rate is governed by alkali concentration, temperature (pressure), grinding fineness and bauxite structure. In some bauxites, aluminium minerals are coated with films of foreign matter, and tend to leach at a slower rate. These bauxites require finer grinding to promote leaching through an increase in aggregate surface area of particles.

Alkali (Na_2O) concentration in the liquor in leaching of diaspore-boehmite bauxites is 300-320 gram/litre, of hydrargillite ones, about 200 gram/litre. The temperatures are 230 and 105°C, respectively.

The reaction leading to the formation of sodium aluminate has been given above. Iron oxides fail to react with the alkali and remain in the red slime.

Vanadium, chromium and gallium pass to solution respectively as vanadate Na_3VO_4, chromite $NaCrO_2$ and gallate $NaGaO_2$. Alkali consumption is low, but impurities tend to gather in recycled liquors and so may contaminate alumina.

Owing to lime additions, titanium remains in red slime chiefly as calcium metatitanate $Ca_2TiO_4 \cdot nH_2O$.

Besides, lime is of use also in that it displaces partly the alkali from sodium alumosilicate deposits.

From the ball mills, the pulp having a liquid-to-solids ratio of about 5.5 is transferred to collecting tanks that are air-tight steel vessels rated to withstand pressures necessary to heat pulp to 250°C*. They are heated by live steam which is injected directly into the pulp and agitates the latter.

Industrial plant autoclaves (Fig. 87) of 24 m^3 capacity, are 1.6 m in diameter and 13.6 m in height. Their walls are heat insulated on the outside to minimize steam consumption and reduce pulp dilution by condensate.

As pulp is discharged from an autoclave, pressure falls off sharply, and this may cause splashing of liquor by the violently evolving steam, this being avoided by discharging pulp into steam separators, available in volumetric and hydrostatic types (Fig. 88). In the former type, superheated pulp boils violently as it enters a narrow inlet and splashes inside the apparatus.

Circulatory steam separators are free from the splashing effect as evaporation takes place in a circulatory pipe as hydrostatic pressure decreases. Resultant steam is used for heating pulps and liquors.

A schematic diagram of a continuous leaching plant (Fig. 89) illustrates the flow of pulp and steam.

From a collecting agitator, pulp enters preheaters, where it is heated by the first-stage separator steam circulating inside the pipes, then passes through 8 to 10 autoclaves connected in series.

Live steam is supplied only to the first two autoclaves at a pressure of 2.5-3.0 MN/m^2 (25-30 atm). Pulp is agitated inside the other autoclaves as a result of continuous flow, while its temperature is maintained by the heat insulation. In the first separator, the pressure falls to 2.0-2.4 MN/m^2 (20-24 atm), and in the second, to 147 kN/m^2 (1.5 atm).

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* Recently demonstrated was a possibility for increasing pressure to 300-320 atm, this reducing leaching time to few minutes.

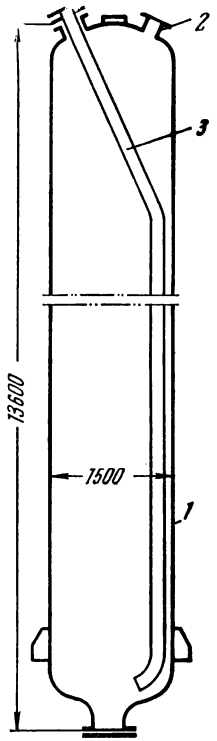

Fig. 87. Autoclave for leaching of bauxite

1—steel thick-walled vessel; *2*—pulp inlet; *3*—pipe for discharging autoclave or transferring pulp to adjacent apparatus

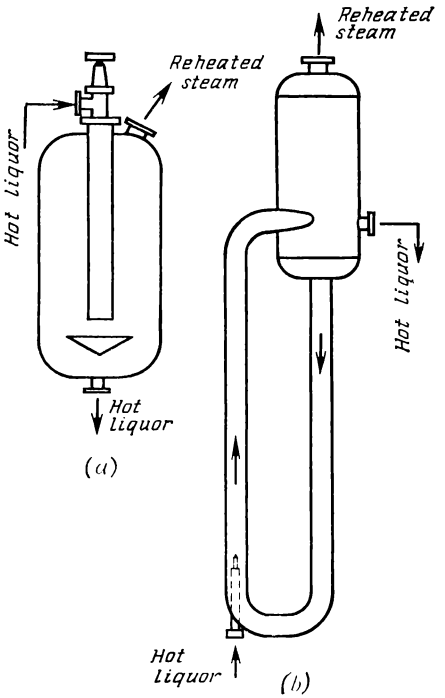

Fig. 88. Steam separators

a—hydrostatic; *b*—volumetric

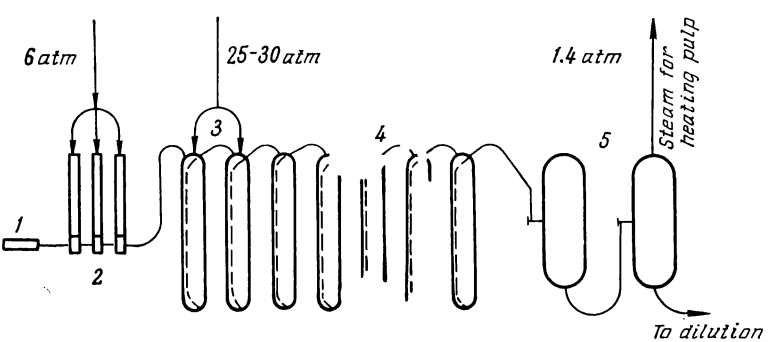

Fig. 89. Continuous leaching of bauxites in autoclaves

1—pulp pump; *2*—pulp heaters; *3*—steam-heated autoclaves; *4*—other autoclaves of bank; *5*—steam separators

Residence time of pulp in autoclaves is 2-3.0 hours.

Hot autoclave pulp is diluted in tanks by waters from washing of red mud and transferred to thickeners for settling, which is slow, particularly that of its finer particles. Additions to pulp of small amounts of flour or starch, and a recent practice, also that of synthetic flocculators, enhances flocculation of colloid particles, improves their coalescence and thus speeds up settling.

After settling and decantation of the bulk of the liquor, the red mud is washed with hot water to scavenge remaining liquor. This is achieved in a system of cascade tanks, or washers, in which pulp flows in a countercurrent direction with respect to the washing liquid (Fig. 90). Pure hot water is supplied to the last washer only, whose overflow passes to a preceding washer, and so on. Overflow from the first washer is utilized to dilute the pulp from autoclaves.

Mud from thickeners, of a liquid-to-solids ratio of about 2, is pumped continuously to the first washer, and, therefrom to the second one, etc. Mud from the last washer is dumped. In thickening and washing, the temperature should not be below 90°C, otherwise hydrolysis is likely to occur, and some alumina may be lost with the red mud. To prevent excessive cooling, hot water is used for washing, and the equipment is heat insulated.

Washing is performed in tray thickeners and washers (Fig. 91), since they require less floorspace and utilize heat more rationally. A tray washer operates similarly to a standard thickener, but is provided with a number of conical bottoms that form chambers. Pulp is fed to each chamber separately, and led out through an individual outlet. Thickened product from all chambers is discharged through an outlet in the bottom. Adjacent chambers are sealed off from one another by a bed of thickened product in the central underflow wells.

After the mud is separated, the liquor still carries about 0.1 gram/litre of solid particles which are removed by filtration in pressure filters through a cloth or in leaf filters through a paper pulp applied against a metallic wire cloth.

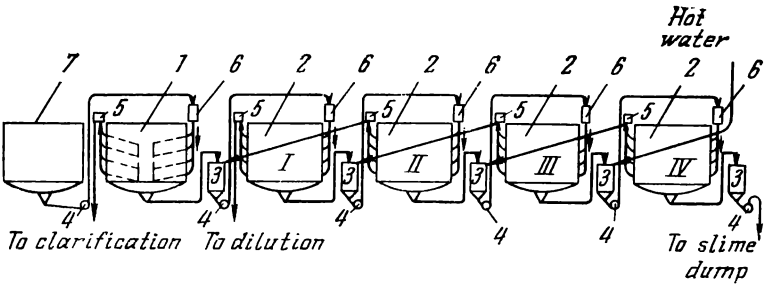

Fig. 90. Four-stage (I-IV) countercurrent washing of slime

1—thickener; *2*—washers; *3*—mixing tanks; *4*—pumps; *5*—discharge boxes; *6*—feeding boxes; *7*—diluted pulp collector

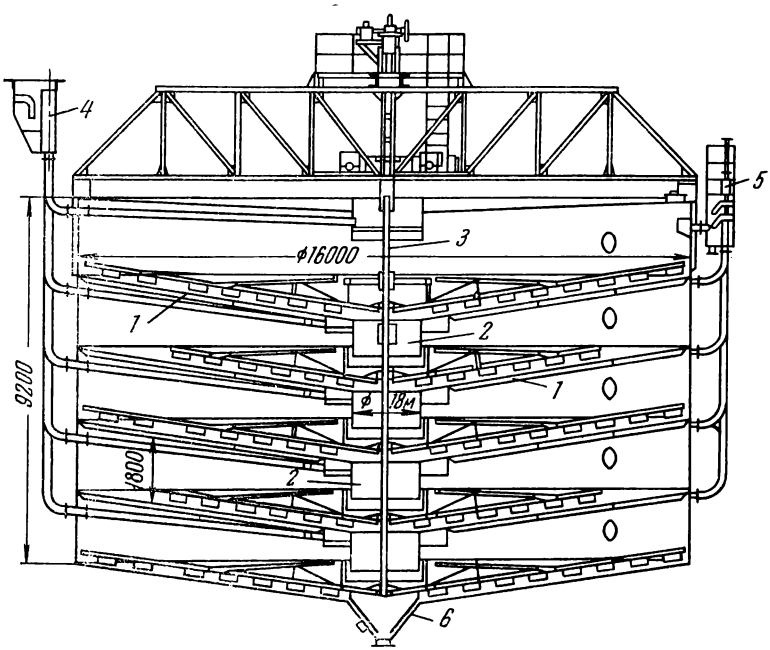

Fig. 91. Tray washer

1—bottoms; *2*—central well; *3*—shaft carrying rake-fitted blades; *4*—feed boxes; *5*—discharge boxes; *6*—conical well for discharge of thickened product

Decomposition of Aluminate Liquor

Filtrated liquor is transferred to decomposition.

The decomposition of the aluminate liquor is an opposite in direction to leaching. It is therefore self-evident that precipitation of sodium aluminate requires dilution of the liquor, cooling, stirring and introduction of a seed.

As it presents ready crystallization centres, a seed speeds up settling of $Al(OH)_3$ and promotes the precipitation of a deposit in the form of readily filterable coarse particles. Rapid settling is also favoured by stirring which maintains particles in a suspended state. The particles are then surrounded at any given time by the liquor, and the solute can thus readily come into contact with surfaces of growing crystals.

The above liquor gives off a precipitate which contains but a part of aluminium. As is readily apparent from the reaction, liquor's alkalinity and caustic ratio both increase as the reaction progresses. The caustic ratio is a molar ratio of the concentrations of free alkali and of aluminium in the liquor. It is also assumed that alkali is in the form of Na_2O (molecular mass of 62) and aluminium, of Al_2O_3 (molecular mass of 102). The liquor run to waste may contain 120 gram/litre of Al_2O_3 and 125 gram/litre of Na_2O, or respectively 120/102 = = 1.18 mole/litre Al_2O_3 and 130/62 = 2.01 mole/litre Na_2O. Caustic ratio of the liquor is then

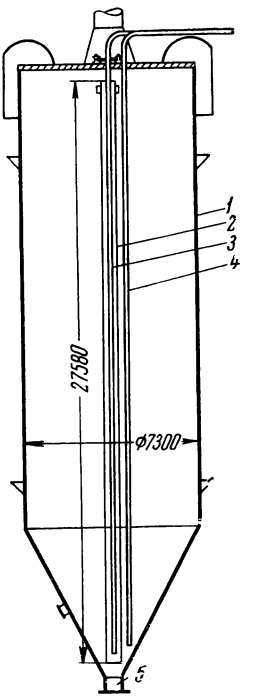

Fig. 92. Air-agitated decomposing tank

1—steel shell with conical bottom; *2*—central pipe; *3*, *4*—pipes for supplying compressed air; *5*—discharge pipe

$$\alpha_c = 2.01/1.18 = 1.70$$

Toward the end of processing the caustic ratio of the liquor rises to 3.4-3.7 because of a decrease in concentration of aluminium that passes to hydroxide deposit.

Aluminate liquors are precipitated in mechanical and, a more frequent practice now, pneumatic agitators, or decomposing tanks, similar in design to Pachuka tanks (Fig. 92). Decomposing tanks, 7 to 8 m in diameter and 25 to 28 m high, are generally connected in series of 9 to 16 units. The liquor runs from one tank to another in a continuous stream, an overall residence time of the liquor in the system being of the order of 60 hours.

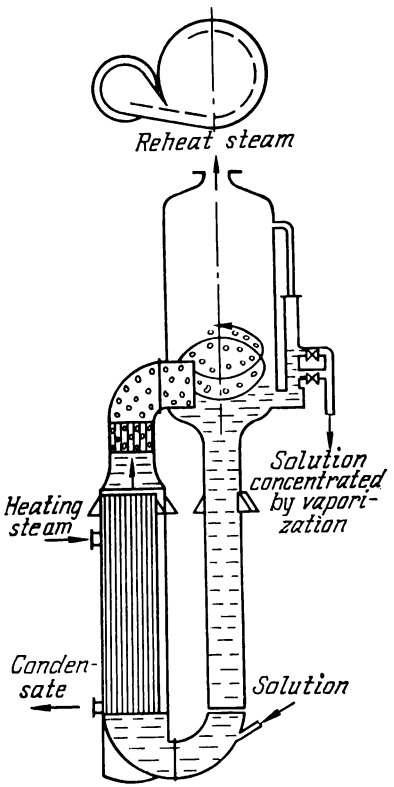

Fig. 93. Vaporizer

Pulp $Al(OH)_3$ from the last decomposing tank is run off to thickeners. Classification of a thickened product yields fine crystals, which serve as seed, while the remaining residue is washed by countercurrent decantation, similarly to red mud.

The quantity of alumina recycled as seed is fairly high, amounting to 80 to 150% of its yield in precipitation liquors (a seed ratio of 0.8 to 1.5).

Washed aluminium hydroxide is filtered in vacuum filters, dried and calcined.

Vaporization of Recycled Liquors and Soda Caustification

Recycled liquors from thickener overflow are vaporized to remove excess water and raise alkali concentration. Vaporizers (Fig. 93) are connected in a series four-unit system that operates under vacuum. The first vaporizer is heated by fresh steam, the others, by saturated steam. In cooling of vaporized

liquor soda, from the interaction of alkali with air carbon dioxide and with carbonates of bauxites, precipitates as crystals.

Crystals of $Na_2CO_3 \cdot H_2O$ are filtered, dissolved in water and turned to NaOH according to reaction (189) by heating the liquor in agitators together with lime milk.

Calcium carbonate deposit is filtered and dumped, while the filtrate is concentrated by vaporization and run off to preparation of raw pulp or to vaporization.

Calcination of Aluminium Hydroxide

Calcination is required to remove water from the $Al(OH)_3$ molecule and thus turn it to alumina according to reaction

$$2Al(OH)_3 \xrightarrow{1200^\circ C} Al_2O_3 + 3H_2O$$

A rotary kiln for calcination (Fig. 94) is a steel pipe, 4.5 m in diameter and up to 110 m long, lined on the inside with fireclay brick. The pipe is set on rolls, sloped at about 3 degrees to the horizon and rotated by a drive at a speed of 1-2 rpm. A fuel oil or natural gas burner is fitted into the discharge (firebox) head at the lower end of the pipe. Aluminium hydroxide moves slowly toward the discharge end in countercurrent with respect to the combustion gases. The kiln is continuously fed with moist aluminium hydroxide and recycled dust at the charging end.

From the kiln hot alumina finds its way to a cooler which is also made in the form of a sloped rotating pipe watered from the outside for cooling purposes.

Combustion gases entrain 50 to 60% of alumina of its amount fed to the kiln, and, therefore, are treated for recovery of dust in dust collectors.

A settling chamber alone is inadequate as regards complete recovery of dust, and, therefore, it is complemented by multi-clones or electrostatic precipitators. As alumina particles are carried away by the gases before they are dewatered, collected dust is mixed with wet alumina and returned to calcination.

Finished alumina is discharged from the cooler through a fine-mesh screen into a bin, then transported pneumatically by compressed air to silo bins of an electrolysis plant.

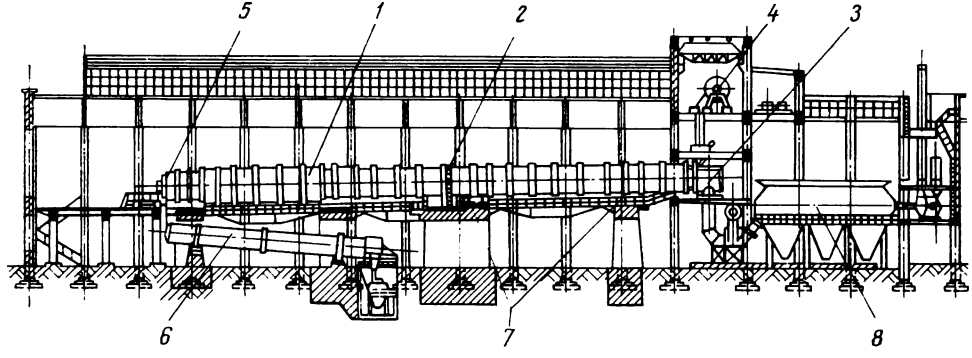

Fig. 94. Alumina-calcination plant

1—rotary kiln; *2*—rotary kiln drive; *3*—charging end; *4*—vacuum-filter; *5*—firebox and discharge end; *6*—alumina cooler; *7*—supporting rollers; *8*—settling chamber

47. Manufacture of Alumina by Sintering Technique

Fusion of Bauxite

After coarse and intermediate crushing, bauxite and limestone are ground in ball mills in recycled soda liquor with additions of fresh soda. The resultant pulp is discharged to conditioning tanks, where its composition is checked and corrected, if necessary.

Fusion is carried out in rotary kilns similar to those used for calcination of alumina.

In the kiln hot zone, the temperature is maintained in the range from 1200 to 1300°C by combustion of atomized fuel oil. The charge, fed to kiln as pulp with about 40% of water, is injected by special atomizers in a countercurrent direction to flow of combustion gases. Splashes of pulp dry while in flight, and solid particles fall and move along the pipe to zones of progressively higher temperatures.

At 900°C limestone decomposes vigorously

$$CaCO_3 \rightarrow CaO + CO_2$$

and, when CaO is subsequently heated to 1100°C, it binds silica in a silicate

$$2CaO + SiO_2 \rightarrow Ca_2SiO_4$$

Formation of sodium aluminate (190) is completed at a temperature below 1200°C, necessary to bind SiO_2 in calcium silicate. In the same operation, soda reacts with iron oxide as well to give sodium ferrite

$$Na_2CO_3 + Fe_2O_3 \rightarrow 2NaFeO_2 + CO_2 \qquad (194)$$

The fused mass enters a cooler, then is transported to bins.

Dust entrained by combustion gases is recovered in dust collectors and returned to fusion.

Leaching Sintered Mass

Sinter fused mass is leached by hot water, care being taken to transfer the maximum amount of sodium aluminate into solution. In the process, ferrite hydrolyzes,

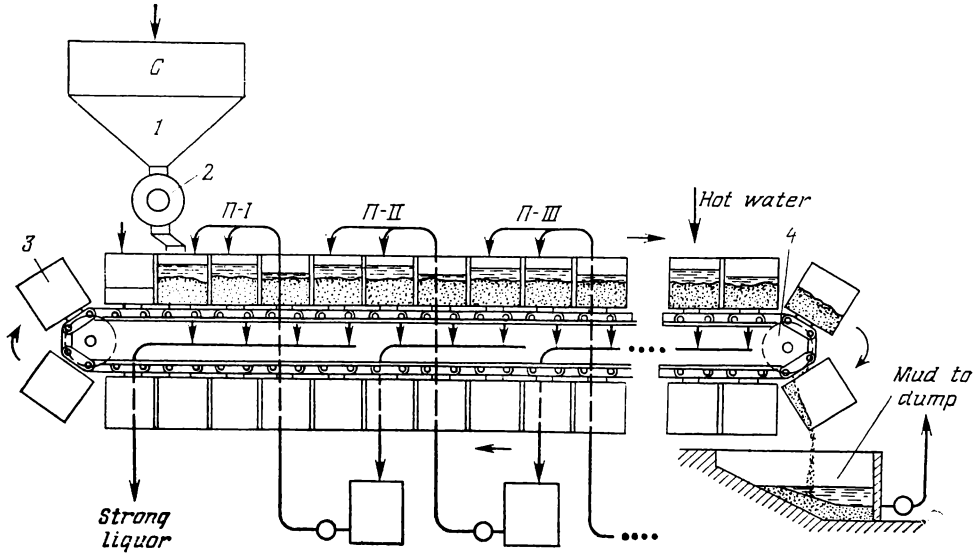

Fig. 95. Continuous percolation leaching apparatus
1—bin for sinter; *2*—drum-type feeder; *3*—percolator; *4*—driving sprockets

freeing the alkali

$$2NaFeO_2 + H_2O \rightarrow 2NaOH + Fe_2O_3 \qquad (195)$$

Adequate leaching of sodium aluminate requires fine grinding and a fairly prolonged stirring with hot water, then séparation and washing of insoluble residue.

All these processing steps are complicated and costly. Besides, they ensure effective recovery of aluminium from low-grade sinters only. Therefore, a frequent practice is to grind the sinter to about 7 mm only and leach it in running liquid in rotary digesters.

A rotary digester (Fig. 96) is a sloped steel pipe, e.g., 60 m long and 3.6 m in diameter, fitted on the inside with a perforated spiral. In rotation, the spiral causes an upward motion of the sinter, while water or an aluminate liquor flows in a countercurrent through the holes in the spiral. Dissolution of sodium aluminate yields heat, and the liquor heats up excessively with the effect that the rotary digester requires cooling, this being ensured either by installing water coolers or by sucking air through the digester to evaporate water and thus provide a cooling effect.

Precipitation conveyer continuous leaching apparatus are similar in design, as regards charging and discharging of solids, to sintering machines, while the circulation of liquors is patterned after that of the gases in sintering.

Prismatic steel percolators with false bottom from a steel screen generally measure 5 × 2 × 2 m, are fitted with wheels and mounted on a frame from rails, similarly to pallet cars of a continuous sintering machine. In other respects, the design and the operation of the apparatus are self-evident from Fig. 96.

At some plants, fused mass is leached by running liquid in diffusors (Fig. 97). Sinter is fed from the top to form a bed up to 5 m on a grate of fine mesh.

Hot water, supplied from underneath the grate, fills the diffusor, percolates through the sinter bed and is discharged at the top. Diffusors connected in series of 12 to 14 units, operate continuously, and liquors flow from one unit to another. Hot water is supplied at one end of the battery, while a strong sodium aluminate liquor is led out at the other end. All diffusors are connected by piping. A

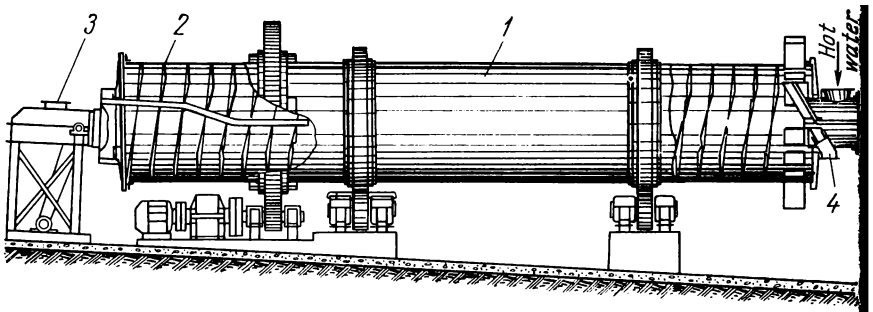

Fig. 96. Rotary digester

1—rotary pipe; *2*—spiral; *3*—device for charging fused mass; *4*—device for discharging slime

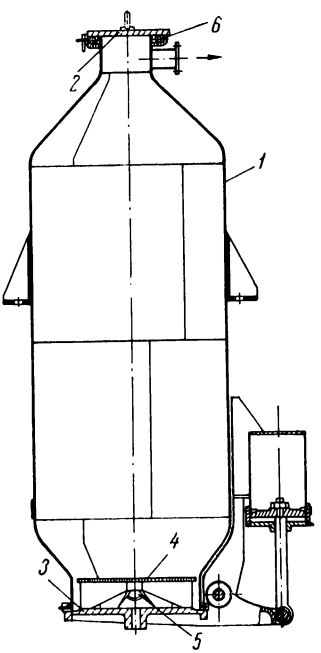

Fig. 97. Diffusor for leaching sintered mass

1—casing; *2*—port for charging fused mass; *3*—swing-away cover for discharge; *4*—grate; *5*—cover hydraulic actuator; *6*—liquor feed

system of stopcocks allows to put any single unit out of operation without interfering with that of the others.

Leaching residue is discharged by opening a port in the apparatus bottom.

Capacities of different leaching apparatus rated to operate on coarse sinter may be compared on the basis of the following hourly productivities, t/h:

Diffusor bank (14 units)	18
Rotary digester	80-90
Percolation apparatus	50-75

Desiliconizing Aluminate Liquors

Sodium aluminate liquors contain from 80 to 240 gram/litre Al_2O_3. Liquors from diffusors carry a maximum of values, whereas those from agitators that treat ground sinter are relatively low grade.

Irrespective of the leaching technique, liquors always carry silicic acid as sodium silicate. Contamination of liquors is described by the silica factor, or the ratio of concentrations

$$\alpha_{si} = \frac{C_{Al_2O_3}}{C_{SiO_2}}$$

The liquor silica factor after leaching is generally below 300, and it should be raised to 450-550 by removal of SiO_2 by heating the liquor in a bank of autoclaves at 160-170°C for 2-3 hours. Heating favours a rapid completion of the reaction between sodium aluminate and sodium silicate

$$2NaAlO_2 + 2Na_2SiO_3 + 4H_2O \rightarrow Na_2Al_2Si_2O_8 \cdot 2H_2O + 4NaOH \quad (196)$$

A similar heating with addition of lime leads to the formation of calcium alumosilicate

$$2NaAlO_2 + 2Na_2SiO_3 + Ca(OH)_2 + 4H_2O \rightarrow \rightarrow CaAl_2Si_2O_8 \cdot 2H_2O + 6NaOH \quad (197)$$

Liquors are desiliconized in banks of autoclaves similar to those used in digesting bauxite by the Bayer process.

Alumosilicates, white slime, are introduced into the sintering charge after thickening and filtration.

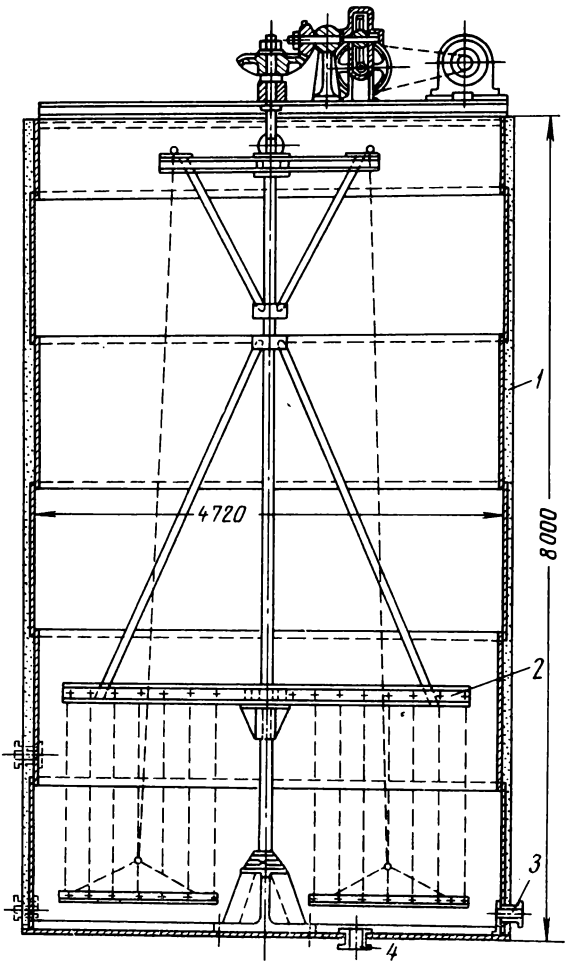

Fig. 98. Carbonizer

1—tank; *2*—chain stirrer; *3*—nozzles for supplying carbon dioxide; *4*—discharge pipe

Carbonization

Carbonization, or treatment by CO_2, decomposes sodium aluminate liquors more effectively than settling and stirring, and brings about an almost complete precipitation of aluminium hydroxide by binding the alkali freed in the hydrolysis into soda.

In order to obtain a hydroxide homogeneous as to size of particles (50 to 80 micrometre), the CO_2 treatment is continued until 95 to 98% of Al are settled out. Combustion gases with 10-12% CO_2 at a temperature of 70-80°C are bubbled through the liquor in carbonizers, the liquor being stirred in the process. The gases are treated for removal of dust prior to entry to carbonizers.

A carbonizer is a steel cylindrical tank up to 6 m in diameter and 8 m high, fitted with gas-injecting nozzles and a chain-type stirrer (Fig. 98). Continuous carbonization in series-connected carbonizers features a high specific productivity and readily lends itself to automation.

Aluminium hydroxide is separated from the soda liquor, washed and calcinated in the same manner as in the Bayer process. Recycled soda liquor is concentrated by vaporization and transferred to preparation of wet sintering charge.

48. Performance Evaluation of Alumina Production Techniques. Combined Flowsheets

The major items of alumina costs are bauxite, processing reagents, fuel and electric power, the other items being relatively small and varying little with the different processing techniques.

Let us first compare the average data on consumption of reagents, fuel and electric power in ton/ton of alumina:

	Alkali	Steam	Fuel	Soda	Limestone
Bayer process	0.09	8.7	0.2	—	—
Fusion method	—	6.4	1.5	0.32	1.5

Alkali is 3 to 4 times more expensive than soda, while limestone is comparatively cheap. Jet fuel costs for the fusion technique, however, are materially higher, thus making the use of this method infrequent.

Bauxite consumption is governed by Al_2O_3 content and recovery efficiency. For example, if a 50% Al_2O_3 bauxite and a 80% aluminium recovery are assumed, 1 ton of alumina will require

$$\frac{1 \cdot 100 \cdot 100}{80 \cdot 50} = 2.5 \text{ ton of bauxite}$$

Losses of aluminium and of alkali in the Bayer process depend on silica content. Therefore, when quality of bauxite is evaluated, account is taken not only of its Al_2O_3 content, but also of that of SiO_2, which is expressed in terms of the silica ratio $\alpha_{si} = \frac{Al_2O_3\%}{SiO_2\%}$. The silica ratio is of no significance for the fusion technique, since silica is bound by lime and has little effect upon Al_2O_3 losses.

Comparison of raw materials costs with other items of the total costs shows that the Bayer process is advantageous for bauxites of $\alpha_{si} > 8$ only. The fusion technique is by far more efficient at $\alpha_{si} < 7$. Combined methods, involving both digesting of bauxite in autoclaves and fusion, have been developed for bauxites whose silica ratio lies between 7 and 8. These methods are known in two basic variants.

In the first of these, a parallel method, it is possible to lower alkali consumption and replace it by a cheaper soda. To this end, one portion of bauxite is digested in autoclaves, while a lesser portion is fused together with soda and limestone. Once leached and desiliconized, the resultant liquor is mixed with that from the autoclaves and both are processed to settle out the hydroxide. Soda that is given off in the concentration vaporization of the recycled liquor is re-used for fusion. Quantities of bauxite fed to each manufacturing strand are calculated in a manner to make up the losses of alkali chiefly by soda.

The parallel technique is advantageous when high- and low-silica bauxites are treated at a single plant.

In the series variant, alkali is replaced by soda and aluminium is recovered to a greater extent from bauxites of low silica ratio. All of the bauxite is leached in autoclaves, and the resultant red mud is fused together with soda and limestone.

Fusion yields sodium aluminate which is formed both from soda that is contained in the charge and from alkali that is contained in the red mud

$$Na_2Al_2SiO_8 + 4CaCO_3 \rightarrow 2NaAlO_2 + 2Ca_2SiO_4 + 4CO_2 \quad (198)$$

Liquors obtained by the autoclave and fused mass leaching are treated together for precipitation. Soda produced by concentration vaporization of recycled liquor is re-utilized in fusion, which eliminates the need for soda causticizing.

The series variant retains the chief shortcoming of the fusion method, namely, a high fuel consumption.

49. Electrolysis of Alumina

Preparation of Electrolyte

The chief component of the electrolyte, cryolite Na_3AlF_6, was initially mined. Deposits of this mineral are very few, and they could not meet the rapid growth of aluminium production, and so the compound had to be synthesized.

In modern practice, cryolite is synthesized from natural fluorite CaF_2. The mineral is ground, dressed by flotation and treated at a temperature of about 200°C by a strong sulphuric acid. The reaction yields a gaseous hydrogen fluoride

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF \quad (199)$$

Contaminating silica reacts with HF to give a volatile SiF_4.

The mixture of HF and SiF_4 is absorbed by water, the effect being hydrofluoric acid HF contaminated by hydrosilicofluoric acid H_2SiF_6.

Salt Na_2SiF_6 is less soluble in water than NaF, and this explains why sodium silicofluoride settles out when soda is added

$$H_2SiF_6 + Na_2CO_3 \rightarrow Na_2SiF_6 + H_2O + CO_2 \quad (200)$$

Once purified and filtered, hydrofluoric acid is treated by a stoichiometric amount of aluminium hydroxide to yield fluoaluminic acid

$$6HF + Al(OH)_3 = H_3AlF_6 + 3H_2O \quad (201)$$

Subsequent neutralization of H_3AlF_6 by soda results in cryolite being formed

$$2H_3AlF_6 + 3Na_2CO_3 \rightarrow 2Na_3AlF_6 + 3CO_2 + 3H_2O \quad (202)$$

Cryolite is poorly soluble in water, and, therefore, it forms a deposit which is filtered and dried.

Neutralization of hydrofluoric acid by a large amount of aluminium hydroxide yields aluminium fluoride

$$3HF + Al(OH)_3 = AlF_3 + 3H_2O \quad (203)$$

Action of soda upon the same acid gives sodium fluoride

$$2HF + Na_2CO_3 \rightarrow 2NaF + H_2O + CO_2 \quad (204)$$

Production of aluminium by electrolysis requires the use of all the above three salts Na_3AlF_6, NaF and AlF_3.

Cryolite Na_3AlF_6 melts at 1000°C, additions of AlF_3 or NaF tend to lower its melting point.

Molten cryolite dissociates as a strong electrolyte

$$Na_3AlF_6 \rightleftarrows 3Na^+ + AlF_6^{3-} \quad (205)$$

Resultant complex anion undergoes a two-step dissociation

$$AlF_6^{3-} \rightleftarrows AlF_4^- + 2F^-$$

$$AlF_4^- \rightleftarrows AlF_3 + F^-$$

F^- ions are also in equilibrium with sodium cations

$$Na^+ + F^- \rightleftarrows NaF$$

Aluminium fluoride possesses a relatively high vapour pressure, its boiling point being 1260°C. If molten cryolite is heated for a while, some AlF_3 tends to vaporize.

Impurities such as Na_2O, H_2O, CaO and SiO_2, specific to cryolite and alumina, decompose molten cryolite according to reactions

$$2Na_3AlF_6 + 3Na_2O \rightarrow Al_2O_3 + 12NaF \quad (206)$$

$$2Na_3AlF_6 + 3CaO \rightarrow Al_2O_3 + 3CaF_2 + 6NaF \quad (207)$$

$$4Na_3AlF_6 + 3SiO_2 \rightarrow 2Al_2O_3 + 12NaF + 3SiF_4 \quad (208)$$

$$2Na_3AlF_6 + 3H_2O \rightarrow Al_2O_3 + 6NaF + 6HF \quad (209)$$

All these reactions may cause the cryolite ratio to rise from its standard value of $3NaF/AlF_3 = 3$ and thus affect the properties of the electrolyte.

Sometimes this phenomenon is reversed as the cryolite ratio drops because NaF is absorbed by the cell lining during the initial period of its operation. The remedy is to introduce some sodium fluoride. Thus, both sodium and aluminium fluorides are required to adjust the cryolite ratio, whose most favourable values lie between 2.6 and 2.8.

Molten cryolite is capable of dissolving alumina which lowers the melt melting point when present in concentrations of up to 15%. Electrolytes with 1.3 to 8% Al_2O_3 are most suitable for the electrolytic manufacture of aluminium.

Calcium fluoride is always present as a contaminant in the cryolite, and as much as 2-3% may accumulate after prolonged operation. This concentration of calcium fluoride lowers the melting point of the electrolyte. A similar and other favourable effects are produced by MgF_2 and NaCl which are added whenever necessary.

To complement the above reaction describing the dissociation of Al_2O_3 in molten cryolite (18), it is well to note that it proceeds in steps, probably in the manner given below

$$Al_2O_3 \rightleftarrows Al^{3+} + AlO_3^{3-}$$

$$AlO_3^{3-} \rightleftarrows AlO^{+} + 2O^{2-}$$

$$Al^{3+} + 2Al \rightleftarrows 3Al^{+}$$

Ions Al^+ are relatively few, as is readily apparent from the value of the equilibrium constant

$$K = \frac{a^3_{Al^-}}{a_{Al^{3+}}} = 6.2 \cdot 10^{-4}$$

As mentioned, dissociation of cryolite (205) may give anions AlF_6^{3-}, AlF_4^-, F^- and others, and also cations Na^+. Since potentials are difficult to measure at high temperatures, the theory of electrode processes is built on the basis of decomposition voltage values, or differences of potentials between anode and cathode which are measured at small current densities and correspondingly small polarization or calculated thermodynamically.

Decomposition voltage of Al_2O_3, measured at temperatures from 960 to 1025°C in a cryolite bath with an aluminium cathode and a carbon anode at small current densities, varies from 1.34 to 1.78 V. These values for AlF_3, NaF, MgF_2, CaF_2 have been found respectively equal to 3.97; 4.37; 4.61; 5.16 V. It follows then that Al_2O_3 is decomposed by electrolysis before other electrolyte components.

The basic reaction at the cathode may be considered $Al^{3+} + 3\bar{e} \rightarrow Al$. Reaction $Al^{3+} + 2\bar{e} \rightarrow Al^{+}$ is also possible, but because of a poor stability of the single-charge ion it has a lesser importance. Oxygen is chiefly reduced at the anode according to a following pattern

$$O^{2-} + xC \rightarrow CxO + 2e$$

where CxO is an intermediate complex of unknown composition whose slow decomposition to CO and CO_2 causes an anode overvoltage of 0.4-0.8 V. Concentration polarization in melts is generally low because of a large diffusion rate.

Power Consumption for Electrolysis

According to Faraday law, the reduction at the cathode of 1 gram of aluminium requires theoretically $26.8/9 = 2.977$ Ah (where 9 is the equivalent mass of aluminium).

Manufacture of one ton of aluminium, assuming a current efficiency of K_e, necessitates a quantity of electricity equal to

$$\frac{2.977 \cdot 10^6}{K_e} \text{ Ah}$$

To calculate the consumption of electric power, this value should be multiplied by the voltage and divided by 10^3 to convert watts into kilowatts. Assuming a current efficiency of $K_e = 0.88$ and a voltage $V = 4.9$ V, we obtain

$$W = \frac{2.977 \cdot 10^6}{10^3} \cdot \frac{v}{K_e} = \frac{2.977}{0.88} \cdot 10^3 \cdot 4.9 \approx 16500 \text{ kW}$$

Some plants operate more economically than others; however, manufacture of aluminium always requires much electric power, whose consumption may be brought down by improving current efficiency and reducing the voltage across reduction cells.

Current Efficiency

It has already been mentioned that a proportion of current is consumed in side processes, such as ones discussed below.

Iron and silica introduced into the electrolyte by its components or transferred from carbon lining and anodes may be reduced at the cathode together with aluminium. They not only call for an additional consumption of electric power, but contaminate the metal as well.

Metallic aluminium is to some extent soluble in the electrolyte. Diffusing throughout the bath and attaining the anode, it is oxidized by oxygen and carbon dioxide

$$4Al + 3O_2 = 2Al_2O_3$$
$$2Al + 3CO_2 = Al_2O_3 + 3CO \qquad (210)$$

the reactions consuming electric power, which is thus lost. Oxidation rate is the greater, the closer is the anode to the cathode (effect of electrode spacing) and the higher the temperature. Bath temperature is also a function of pole spacing, as the latter's increase raises the electric resistance between the electrodes and thus causes a corresponding rise in temperature. Accurate control of these mutually dependent electrolysis conditions requires the use of automatic devices.

Voltage Across Reduction Cell

Another cause of high power consumption of energy in electrolysis of aluminium is related to voltage across the reduction cell.

Let us multiply the equation (33) term by term by the current intensity and time. We obtain

$$I \cdot V \cdot t = W = (E_a - E_c) I \cdot t + I^2 \cdot R \cdot t \qquad (211)$$

Power consumption thus consists of two parts. The former concerns the electrolysis, and the latter is consumed in heating of the electrolyte, i.e., it expresses the Joule law. In aqueous solutions where currents passing through the electrolyte are of the order of thousands of amperes, the loss of electric power in heating is fairly small. In melts at temperatures of about 1000°C, currents often exceed

100 000 A, and about 2/3 of electric power are lost in heating of reduction cells. The chief factor here is the electrode spacing which determines the thickness of the body of electrolyte between electrodes. The greater the spacing, the greater the electrical resistance and the voltage drop. At the same time, closer spacing of electrodes brings about a drop in current efficiency because of an intensive oxidation of aluminium. Practice has shown optimum spacing to be between 4 and 5 cm. Spacing is adjusted automatically on the resistance of the body of electrolyte between the electrodes.

Voltage may also be reduced by increasing the electrical conductivity of the melt through greater cryolite ratio or by increasing the temperature. However, both these means involve loss of current due either to a simultaneous discharge of Na^+ ions or intensive oxidation of aluminium at the anode. Overheating favours vaporization of AlF_3.

Addition of NaCl or $MgCl_2$ raises melt electrical conductivity, while that of CaF_2 and MgF_2 lowers it. All these additives have little effect upon voltage, if their aggregate content is below 10%, while their usefulness lies in that they lower the solidification point of the electrolyte and the temperature of electrolysis, reducing current losses related to overheating of the cell.

Current Density

Current density is both the ratio of current intensity in amperes to the surface area of cathode in square centimetres and a measure of cell productivity.

A greater amount of metal can be obtained from a cell by increasing current density. However, the greater the current density, the higher the voltage across the cell and the greater the quantity of energy consumed in electrolysis. Optimum cathode current density, found from years of practice, averages 0.75 A/cm^2.

Anode Effect

As already has been mentioned, gases evolve at the anode, while oxygen combines with carbon of the anode to give CO and CO_2. If molten electrolyte wets adequately the carbon

anode, gas bubbles off readily, whereas, if the wettability is poor, the gases tend to form a continuous gas layer (Fig. 99).

Wettability is affected by Al_2O_3 content in the electrolyte. As long as there is much alumina, anode wettability is

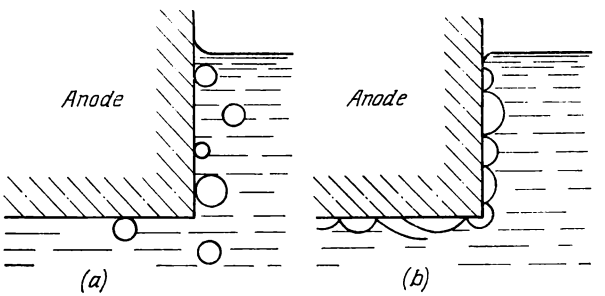

Fig. 99. Formation of gaseous film on carbon anode in the anode effect
a—gas bubbles formed in normal electrolysis; electrolyte is cryolite +10% of alumina; *b*—formation of gaseous film causing anode effect; electrolyte is cryolite +0.5% alumina

high, but when Al_2O_3 content comes down to less than 1%, it falls off sharply, the anode and the electrolyte then being separated by a gas interlayer, which is poor conductor of electricity, with the effect that the cell circuit resistance rises rapidly, as does the consumption of electric power.

In order to detect in good time the anode effect, a lamp rated at 30-40 V is connected in parallel with the cell. In normal operation, the lamp gives no light as the standard voltage across the reduction cell is insufficient to produce incandescence of its filament. Should the anode effect arise, the voltage rises, and the lamp lights up.

Anode effect is a signal for charging a fresh portion of alumina, but it also means a sharp increase in voltage, and, consequently, in electric power consumption and, in the final analysis, in costs. Therefore, care is taken to keep the frequency of anode effects to not more than one or two a day by appropriate charging of alumina.

Design of Reduction Cell and Its Operation

Carbon items required for building the reduction cells, rectangular blocks, plates and anode mass (the material of anodes), are manufactured at specialized plants. The raw materials are low-ash carbon materials, as, some varieties of anthracite, petroleum and pitch coke. If ash content is not kept sufficiently low, its components may dissolve in molten electrolyte and thus contaminate aluminium or lower current efficiency. Petroleum and pitch coke are products of dry distillation of petroleum or coal pitch. Ash contents of both these materials approximate 0.4%, while in anthracite it amounts to 3-5%. Anthracite is suitable for less critical items, such as plates and blocks.

Petroleum and pitch cokes and anthracite are crushed and burned at 1300°C to remove volatiles as fully as possible. Cooled materials are ground, screened, mixed in predetermined size proportions, first, one with another, then with hot pitch. Pitch, a viscous coal tar distillation residue, acquires sufficient fluidity at 45-85°C and is moulded into items at pressures between 24.6 and 39.2 MN/m^2 (250-400 kgf/cm^2). Mechanical strength is enhanced and porosity is reduced by baking at 1400°C, the temperature being slowly raised to this point, then as slowly lowered to a predetermined schedule after a specified holding. Overall baking time is about 200 hours. The pitch cokes, and the items thus become strong and solid. Compressive strength of baked carbon items attains 24.5-34.3 MN/m^2 (250-350 kgf/cm^2), whereas the porosity is below 25%.

The carbon-item manufacturing plants, also produce anode mass briquettes, or non-baked mixture of carbon powders with a small content of binding pitch.

To complement the description of an aluminium reduction cell, schematically illustrated in Fig. 84, it is well to mention that it rests on a concrete foundation covered with a few courses of brick. The hearth is from carbon blocks, parallelepipeds measuring 400 × 400 × 550 mm, and walls, from carbon plates. The walls are reinforced on the outside by brickwork, a filling of fire clay and enclosed for strength in a ribbed steel casing. Hearth blocks are provided with

grooves. Steel rods are placed inside these grooves and poured with cast iron. The rods are connected to busbars that supply the current.

An anode is encased in sheet aluminium about 0.9 mm thick and suspended from a steel construction above the reduction cell. Anode mass is charged into the casing. The mass heats up, melts, then thickens and hardens.

Bottom layers of the mass, that dip into the electrolyte, bake to form a "baking cone" shown in Fig. 84. As the anode burns away, it is gradually lowered with the aid of an appropriate mechanism, the end of the aluminium casing melting in the process. Fresh anode mass is added at regular intervals into the casing.

Current is supplied to the anodes by steel rods arranged in four horizontal rows (two of these are shown in the illustration). Two bottom rows of rods are the working ones, they serve to supply the current and to attach the anode to its suspension. As the anode burns away and is lowered, bottom rods are pulled out by a pneumatic device and driven into the rows above which now become working ones.

An anode of the above type is termed continuous, self-baking, with side supply of current. Use was formerly made of pre-baked carbon electrodes which were built-up with fresh sections as they burned out. Self-baking anodes have proved to be more attractive economically and convenient in practice. Their use has now become a standard practice even in electric furnaces, e.g., in smelting of nickel mattes. Some plants have again returned to baked carbon anodes because of the simpler cell design and absence of resinous volatile matter. There are also reports of cells being equipped with continuous baked anodes, built-up of ready-to-use lengths carrying holes for current supply rods and set in place with the aid of anode mass inserts.

Size and productivity of a reduction cell is described by its electric power rating or current intensity rating (load in amperes). Ampere load of modern small cells is 30 000-40 000 A, of medium ones, 50 000-80 000, and of large ones, 100 000-150 000 A.

The necessary anode underside surface area and geometric dimensions of a cell may be determined on the basis of

a standard current density of 1 A/cm² or 10 000 A/m². The required anode surface area for a load of 100 000 A will thus be 100 000 : 10 000 = 10 m².

Current supply rods cannot be driven very deep, and anode width is thus limited by uniformity in current distri-

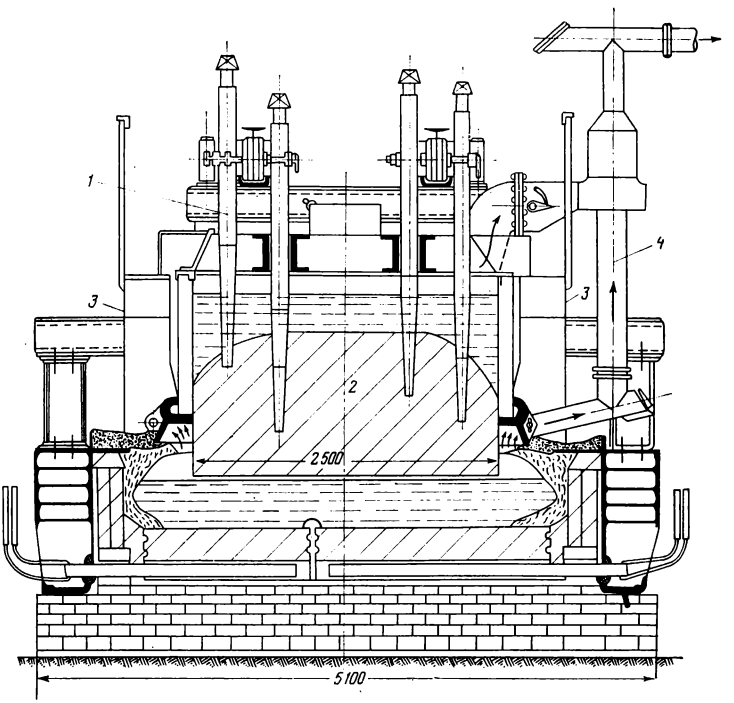

Fig. 100. Aluminium reduction cell with top-mounted current supply rods

1—rods; *2*—baked portion of anode; *3*—iron blinds; *4*—gas suction flow

bution, while total load upon a cell is dictated by its length. If rods are driven in from the top, a wider anode can be obtained, and the cell's productivity can be increased.

In cells with a current supply from the top rods are inserted into the anode from the top and arranged in 2 to 4 rows at various levels in height (Fig. 100).

The cell is provided with extensible or lift-up side iron blinds intended to suck out noxious anode gases.

With a lateral current supply arrangement, as the rods occupy much space, the blinds are at some distance away from the anode with the effect that much atmospheric air is sucked together with the gases. With top-mounted current supply rods, the suction arrangement is simpler, and the noxious gases, which are thus not too much diluted with air, can be burned.

Still another advantage inherent in the top-mounted current supply rods is a possibility to dispense with the anode aluminium casing. The latter, which requires continual build-up, can be replaced by a fixed steel one, inside of which the baked anode slides down.

Top-mounted current supply cells are being used on an ever growing scale owing to simplicity of design and mechanized operation.

Mercury rectifiers rated for 10 000-20 000 A and up to 1100 V are standard current supply equipment for aluminium-reduction cells. Silicon semiconductor rectifiers rated for up to 25 000 A and 450 to 850 V have been introduced industrially in recent years. Efficiency of the former is 92-95%, that of the latter, up to 97%.

A 150 000 A cell will thus require six parallel silicon rectifiers. Depending on power supply voltage, the series circuit includes 140 to 160 reduction cells. When the number of cells is calculated, account is taken of losses (voltage drop of 1% in the line from a substation, possible voltage variations of 5% in the outside circuit) and 40 V are added to compensate for anode effects.

For example, a cell series supplied from a 700-V silicon rectifier requires 4.6 V per cell. The series can thus be built up of

$$N = \frac{700 - (700 \cdot 0.06 + 40)}{4.6} = 134 \text{ cells}$$

Number of cells in a series generally lies between 140 and 160.

Rectifiers are housed in a separate building near the electrolysis plant. A stand-by rectifier is provided for each four operating ones.

Cell series are arranged inside two elongated buildings set parallelly about 40 m one from another.

Aluminium-Reduction Cell Practice and Supervision of Operations

After placing into service or overhaul, a cell is expected to operate continuously for 3 years. Electrolyte surface in a normally operating cell is covered by a solid crust. Alumina that is conveyed to cells by pneumatic or other means

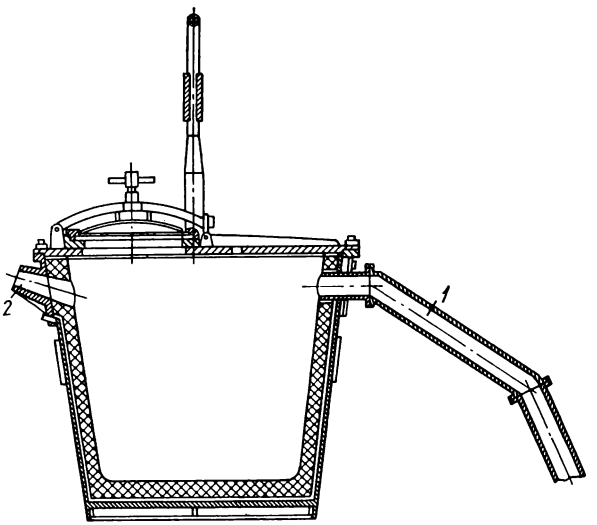

Fig. 101. Vacuum ladle for discharging molten aluminium from cells
1—pipe for sucking in molten aluminium; *2*—pipe for vacuum build-up

is charged upon the crust, and charging proper is performed by breaking up the crust with the aid of a special mechanism.

Alumina is charged at required intervals of time, in accordance with the operating schedule and the progress of electrolysis. Care is taken to keep the electrolyte adequately high in alumina and to avoid anode effects which cause excessive power consumption. If a cell is operated correctly, anode effect is liable to occur not more than once every 1 or 2 days.

Thickness of electrolyte layer should be kept within 17 to 20 cm. It is measured by dipping an iron rod into

the cell and maintained at required value by timely charging of cryolite.

Cryolite ratio is checked by analysis at regular intervals of time and corrected, whenever necessary, by addition of sodium fluoride, of aluminium and of various other substances. Fluorides and cryolite are charged similarly to alumina.

Accumulation of aluminium on cell bottom decreases the electrode spacing, while too frequent a tapping of aluminium is undesirable because of heat losses and a host of other reasons. Aluminium is discharged from cells once every 2 to 4 days by means of a vacuum ladle (Fig. 101), a layer of molten aluminium not less than 20-25 cm thick being left in the cell.

Cell Temperature Control

The temperature inside the cell is generally in the 940 to 960°C range, various departures from these limits being possible. An excessively cold or hot run of cell is indicative of incorrect electrolysis conditions and high power consumption, and, therefore, it should be remedied to rapidly.

A cold run may be caused by too small a current intensity, small interelectrode spacing, too large a quantity of aluminium in the cell. Inadequate heat supply in case of a low current intensity needs no comment. As mentioned above, a lesser spacing of anode and cathode lowers the voltage drop across a layer of electrolyte, and, consequently, the quantity of heat given off by the current. Too high a layer of aluminium raises heat transfer to the outside medium. A cold run of cell is made worse by deposits in the electrolyte chiefly near cell walls. Accretions push the molten metal toward the centre and raise its level, thus bringing the electrodes still closer together. All this may cause a complete freezing of the cell.

In addition to increasing the interelectrode spacing, a cold run may be corrected by tapping out some aluminium or pouring some hot electrolyte from an adjacent cell.

A small interelectrode spacing may also cause a hot run of cell because of intensive oxidation of aluminium at its anode, since oxidation gives off much heat.

Local overheating is not infrequent, the causes being, among others, broken pieces of anodes or lining, accretions in the electrolyte, non-uniform oxidation of anode.

A hot run is corrected after the causes are tracked. The general remedies are addition of solid or molten aluminium, adjustment of electrode spacing and of electrolyte level.

Treatment and Casting of Aluminium

Aluminium that is withdrawn from a reduction cell is contaminated by non-metallic impurities such as electrolyte inclusions, particles of coal and refractory materials and dissolved gases, chiefly hydrogen. Overheated molten aluminium vigorously reduces hydrogen which has been introduced into the cell with water and air moisture. Gaseous hydrogen is dissolved in aluminium. Non-metallic impurities and gases are removed from aluminium by chlorination, which is carried out in a special ladle lined on the inside with refractory brick. Molten aluminium from a cell is poured inside the ladle. The ladle is placed under a bell, a graphite pipe is immersed into the metal and chlorine is blown through it to oxidize a small amount of aluminium according to reaction

$$2Al + 3Cl_2 \rightarrow 2AlCl_3 \qquad (212)$$

As chlorination proceeds, temperature of the metal in the ladle is about 750°C.

Aluminium chloride evolves as vapours, as its boiling point is 180°C. Chloride bubbles float in molten aluminium and entrain non-metallic inclusions and dissolved gases.

To settle out impurities and to average composition of metal from a number of tappings, aluminium is poured inside electric furnaces whose baths are heated to 690-730°C by nichrome strip resistors suspended to the roofs. These furnaces operate on a batch basis, metal is cast from it every 7 to 10 days and the bath is thoroughly cleaned of slag and oxides.

Aluminium is cast in conveyor casting machines, 9-10 m long, fitted with continuous chains that carry moulds at a linear speed of 1—1.5 m/min. Solidification of metal is

speeded up by blowing with air, and at the discharge end the moulds strike a stop and turn over to dump aluminium ingots.

Metal may be cast into special shapes, wirebars that are intended for wire manufacture, and into ingots for working by rolling. A semi-continuous casting technique is both productive and economical.

Electrolytic aluminium corresponds to grades (the USSR State Standard GOST 11069-64) containing 99.0-99.85% Al.

50. Economics of Aluminium Production

Chief tasks facing the aluminium industry are higher cell productivity and lower aluminium costs.

Cell productivity depends on current intensity and efficiency.

Increases in cell size and power rating, e.g., replacement of 65 000-A cells by ones of 130 000 A, involve adjustment of electrolysis conditions. Relative heat losses of a large cell are less than those of a small one because of a smaller surface area that gives off heat to the atmosphere. Overheating of the electrolyte may cause rapid vaporization of AlF_3, and a decrease in current efficiency because of appreciable oxidation of aluminium.

Cell productive capacity rises with current density, but the temperature of the electrolyte and the power consumption increase as well due to greater voltage across the electrodes.

Current efficiency is governed by many factors, inclusive of current density and cryolite ratio in the electrolyte. A raise in current density results in improved current efficiency in relatively acid electrolytes that possess a high electrical resistance. It follows then that an improvement in current efficiency is paralleled by a rise in voltage across cells and an increase in power consumption.

Electrolysis parameters are closely interrelated and exert a combined action upon the consumption of electric power, and, therefore, any change in cell productive capacity calls for performance calculations and sometimes field testing, otherwise it may prove to be disadvantageous because of increased cost of aluminium.

Consumptions of alumina and of electric power are the largest items of the aluminium costs. As mentioned, consumption of the latter is greatly affected by electrolyte composition, current density, electrode spacing and cell operation. Modern plants consume from 57.6 to 31.2 gj (16 000 to 17 000 kWh)* per ton of aluminium. This parameter is sometimes expressed by the quantity of aluminium in grams produced per kilowatt hour and is termed yield of metal on power consumption. Its value lies between 60 and 62 gram/kWh.

Chief items in aluminium costs are raw materials, fluoride salts and carbon manufactured items.

Alumina consumption can be lowered by minimizing losses in transportation and charging. Fluoride salt requirements depend on electrolysis conditions and quality of alumina. Savings on fluorides can be obtained by conducting the electrolysis at low temperatures and preventing anode effects. It is of a great advantage, but practically still a problem, to collect fluorides from gases evolving from cells. Contamination of alumina by alkali, moisture and silicon dioxide causes losses of fluorides because of decomposition according to the reactions discussed above.

51. Manufacture of Extra Pure Aluminium

Some branches of new technology call for aluminium containing a minimum of impurities. It corresponds to grades A99-A999 of the relevant USSR State Standard GOST specifications. Extra pure aluminium possesses high electric conductivity, resistance against corrosion and light reflectivity. It is used in the manufacture of special chemical apparatus, electrolytical capacitors and light reflectors. Aluminium of 99.999-99.9999% purity is used in radar equipment, in nuclear power production and semiconductor materials industry.

Extra pure aluminium is obtained from standard metal by removing iron, silicon, titanium, copper and other contaminating elements. This is achieved by various methods, depending on requirements upon the purity of aluminium.

* gj is gigajoule; 1 gj = 10^9 j.

Electrolytic Refining in Three-Layer Cell

In this technique, aluminium is treated by electrolysis at 760-800°C in a melt containing 60% $BaCl_2$, 17% NaF, 23% AlF_3; 5% NaCl. Melt density is around 2700 kg/m³. Pure aluminium, whose density under given conditions is

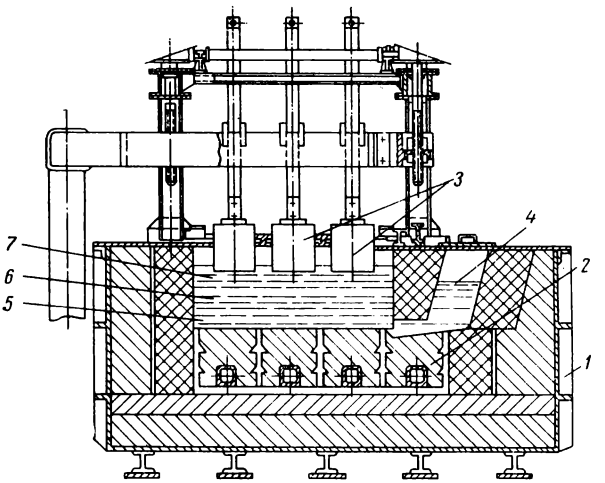

Fig. 102. Aluminium electrolytic refining cell
1—casing; *2*—carbon blocks; *3*—baked carbon cathodes; *4*—pocket for charging aluminium; *5*—anode alloy; *6*—electrolyte; *7*—pure aluminium

2300 kg/m³, floats over the melt. Starting contaminated metal is required to sink in the melt, and to this end it is alloyed with about 30% by mass of copper. The density of this alloy is 3000 to 3500 kg/m³.

The arrangement of liquid layers in a cell is shown in Fig. 102. The bottom layer is the anode, and the top layer, the cathode. The positive pole of a DC source is connected to the former, and the negative one to the latter.

As in a customary electrolysis, metals dissolve at the anode, i.e., turn to ions, which give off their charges at the cathode to form atoms of metals. The more electronegative anode alloy elements, alkali and alkali-earth metals and aluminium, pass to ionic state, while ones more electropo-

sitive than aluminium, silicon, iron and copper, remain in the alloy. Ions reach the cathode through diffusion, and ones highest in electropositive value, namely, ions of aluminium, give off their charges, while those of greater electronegative potential remain in the electrolyte.

To implement the process industrially, use is made of reduction cells with baked carbon cathodes. The cell bottom is of carbon blocks, and the walls of magnesite brick. Aluminium to be refined is poured into the side pocket and enters the lower part of the melt where it mixes with anode alloy.

Charging is adjusted in a manner to maintain the thickness of the bottom layer at around 250 mm. Refined aluminium accumulates over the electrolyte, whence it is withdrawn at regular intervals so as to keep the layer about 100 mm thick.

Refining of aluminium of standard purity (99.5-99.7%) in a three-layer cell yields 99.9965% pure aluminium which finds use in electrical engineering, chemical and foodstuff industries. Refining is costly, since the voltage across the cell is high (5.56 V), as is the power consumption. Despite a high current efficiency (95-98%), power consumption ranges from 18 000 to 19 000 kWh per ton of aluminium.

Zone Melting

Treatment of electrolytic aluminium by zone melting may yield a metal of 99.9999% purity.

This method is even more costly than electrolysis and less productive. Zone melting is applied to small quantities of metal for the manufacture of semiconductors and other critical applications.

After refining by electrolysis, aluminium is cast into rods 15 to 20 mm in diameter and about 300 mm long, and a single rod is placed in a boat of very pure graphite.

The boat is introduced into a quartz tube, where a vacuum is built up of a residual pressure of the order of $133.3 \times \times 10^{-4}$ N/m^2 (10^{-4} mm Hg). Vacuum prevents the oxidation of the metal (Fig. 103).

A loosely-fitting mobile annular inductor, a turn of copper pipe connected to a source of high-frequency current, is passed over the tube. When the turn surrounds the rod of

aluminium that part of the rod that is against the turn carries an induced current (eddy currents).

Heat given off by the current is adequate to melt aluminium opposite the turn, while the remaining part of the rod remains solid. The inductor turn moves along the rod at

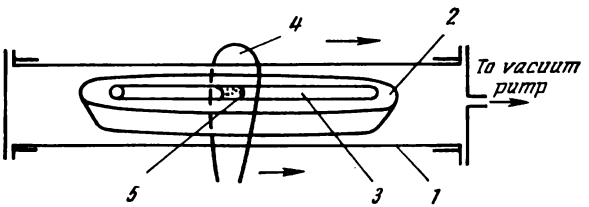

Fig. 103. A schematic diagram illustrating refining of aluminium by zone smelting

1—quartz tube; *2*—boat; *3*—aluminium rod; *4*—inductor turn; *5*—melt zone

a rate of, e.g., 1 mm/min, as does a molten zone 10 to 15 mm long. Impurities concentrate in the melt and move with it towards the end of the rod.

After 10 to 15 such passes, the rod is removed and a length of 8-10 cm is cut from the end which was processed last. The remaining part of the rod is aluminium of highest purity.

Review Questions

1. What kinds of aluminium raw materials are processed by the Bayer and the fusion processes?

Nepheline, kyanites, bauxites, high-silicon bauxites, alunites, kaolins and clays.

2. At what temperatures is Al_2O_3 treated in the alkali autoclave and fusion with soda processes?

60, 375, 160, 200, 600, 1000, 1200°C.

3. What reagents are consumed in large quantities in the production of alumina by the Bayer and the fusion processes?

Alkali, soda, lime, limestone.

4. Name chief constituents of electrolyte for production of aluminium and compounds that serve as additives.

AlF_3, MgF_2, CaF_2, Al_2O_3, Na_3AlF_6, NaF, NaCl.

5. Name causes of a reduced current efficiency and increased voltage across the cells.

Increase in electrode spacing, drop in temperature of electrolysis, formation of AlF_3, presence of such impurities as Na_2O, H_2O, SiO_2, and dissolution of aluminium in the electrolyte.

6. What impurities are removed from aluminium in three layer refining?

Na, Fe, Si, non-metallic inclusions, H.

CHAPTER 8

METALLURGY OF MAGNESIUM

52. Chemical Properties of Magnesium and of Some of Its Compounds

Magnesium is an element of group II of the periodic table of elements. Its metallic properties are more clear-cut than those of aluminium and beryllium, although to a lesser degree than those of lithium and calcium. Magnesium is always divalent. Magnesium's electrochemical potential is

$$Mg^{2+} + 2e \rightleftarrows Mg; \quad E^0 = -2.4 \text{ V}$$

Despite a high negative value of the potential, magnesium decomposes cold water but very slowly according to reaction

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \qquad (213)$$

the reason for this being the formation on its surface of a poorly soluble hydroxide. Hydrogen evolves at a higher rate when the above reaction is conducted in hot water, in which magnesium hydroxide is more soluble, and violently when magnesium is brought into contact with acids, even very dilute ones.

Magnesium is stable in dry air only, as moisture loosens the surface oxide film and opens access for oxygen. Impurities sharply affect corrosion resistance of magnesium.

Magnesium strip or powder can easily be ignited to burn vigorously in the air with the formation of a fine white oxide powder according to reaction

$$2Mg + O_2 \rightarrow 2MgO \qquad (214)$$

The reaction gives off much heat and light. Formerly, combustion of magnesium was put to use in photography and pyrotechnics, while today it is employed in military engineering for flares, incendiary and marker projectiles and bombs. When in ingots or lumps, magnesium fails to ignite,

but it may inflame spontaneously in the process of melting. This is prevented by melting it together with a flux composed of a mixture of KCl, NaCl and other salts.

Magnesium oxide is refractory, its melting point being 2500°C. As mentioned, magnesium oxide, obtained by burning natural magnesite $MgCO_3$, is widely used for the manufacture of refractory brick.

Owing to magnesium's great affinity for oxygen, its oxide can be reduced by carbon at a temperature of about 2500°C only. Magnesium's boiling point is 1107°C, and, therefore, it is readily apparent why its reduction by carbon results in vapours of the metal.

Affinity of magnesium for sulphur is appreciably lower than that for oxygen. Magnesium sulphide is soluble in water and hydrolyzes readily

$$MgS + 2H_2O \rightarrow Mg(OH)_2 + H_2S \qquad (215)$$

This explains why no MgS occurs naturally.

Magnesium also possesses a high affinity for halogens, and magnesium fluoride and chloride are very stable compounds. This is made use of in metallurgy for metallothermic reduction of halides of metals (19, 20).

53. Raw Materials for Manufacture of Magnesium

Magnesium occurs in sizable amounts in the earth's crust, its clark being 2.35%. An appreciable stock of magnesium is in sea water which averages 0.3% $MgCl_2$, 0.04% $MgBr_2$, 0.18% $MgSO_4$. According to approximate calculations, hydrosphere accounts for $1.85 \cdot 10^{15}$ tons of magnesium, but due to a low concentration its recovery from sea water is costly and is employed in countries which have no other raw materials (USA, Norway, Britain).

Some salt lakes, e.g., Evpatoriiskoye, Sasyk-Sivashskoye, Sakskoye and others, and water of sea gulfs, as, Kara-Bogaz-Gol and Sivash, carry large concentrations of magnesium, but its extraction there is less advantageous than that from salt deposits.

Magnesium compounds, such as carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$, magnesite $MgCO_3$ and dolomite $MgCO_3 \cdot CaCO_3$ which are suitable for the manufacture of the metal, are plen-

tiful in our country. In the USSR, about 80% of magnesium are extracted from carnallite and 20% from magnesite.

Carnallite is a hygroscopic mineral salt containing along with magnesium, some potassium and such impurities as sodium chlorides and bromides. Mined ore is termed carnallite rock or natural carnallite. It contains, e.g., 19% KCl, 25% $MgCl_2$, 24% NaCl, 30% H_2O and 2.4% of insoluble residue.

Natural carnallite is treated by a hydrochemical dressing technique based on a lesser solubility of NaCl as compared to KCl and $MgCl_2$. Crushed rock is dissolved at 110°C in a recycled liquor of magnesium chloride (~32% $MgCl_2$). The bulk of NaCl remains as crystals and is separated on screens. Liquor is transferred to vacuum crystallizers. Resultant crystalline pulp is settled in thickeners, then centrifuged to yield artificial carnallite of the following composition, %: 32 $MgCl_2$, 25 KCl, 6 NaCl, and 37 H_2O.

Recovery of magnesium to artificial carnallite is 75% at the most, and a search is going on for other more advantageous processes, in particular, those based on mechanical ore dressing.

In contrast to the standard technique, vacuum crystallization is more productive, but yields relatively fine crystals.

Supersaturation in the apparatus is achieved by vaporization of the solvent simultaneous with the cooling of the liquor.

As mentioned, boiling point depends on outside pressure, and decreases with the latter. For example, the relationship between the boiling point of water and pressure may be described by the figures below:

p, kN/m² (mm Hg) ...	101.31 (760)	12.33 (92.5)
t_{boil}, °C	100	50
p, kN/m² (mm Hg) . .	3.27 (23.8)	1.23 (9.2)
t_{boil}, °C	25	10

Above liquors tend to boil at somewhat higher temperatures than water, but this difference is generally in units of degrees. In a vacuum crystallizer, water vaporizes intensively carrying with it much heat as latent heat of vaporization, the liquor cooling in the process.

Batch-type and continuous vacuum crystallizers are used today on an industrial scale, and in many applications they are more productive and economically attractive than standard crystallizers.

54. Magnesium Manufacturing Techniques

Metallic magnesium was obtained for the first time by Davy in 1808. Davy treated an aqueous solution of magnesium salt by a mercury-cathode electrolysis and obtained an alloy of mercury and magnesium, or an amalgam. Vaporization of mercury gave a small amount of metal, highly contaminated by impurities.

At a later date (1852), Bunsen extracted magnesium by electrolysis of molten chloride, and this served as a basis for an industrial manufacture of magnesium alloys (1908).

Electrolysis of Molten Chloride

Electrolysis of molten chloride $MgCl_2$ or of a $MgCl_2$ and KCl melt has now become the standard practice over the world. A schematic diagram of a cell used for this purpose is shown in Fig. 104.

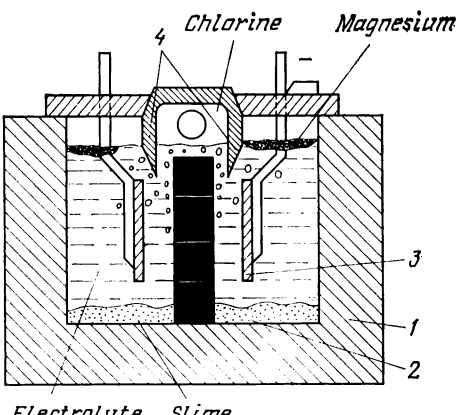

Fig. 104. Cell for electrolysis of magnesium
1—cell of steel-encased refractory brick; *2*—graphite anode; *3*—steel cathode; *4*—membrane

A graphite anode is placed in the middle of the cell, and at the sides, two steel cathodes. Magnesium chloride melts at 718°C, and the melt consists of ions Mg^{2+} and Cl^-.

Ions Mg^{2+} discharge at the cathode (17) and magnesium, given off in molten state (melting point 651°C), floats over the electrolyte. Density of molten magnesium is about 1.47, and that of molten $MgCl_2$, 1.68.

Chlorine evolves at the anode (18), its bubbles floating in the electrolyte. Magnesium and chlorine should be effectively separated, otherwise magnesium is liable to burn in chlorine

$$Mg + Cl_2 \rightarrow MgCl_2 \qquad (216)$$

Ceramic partitions, membranes, are fitted in the reduction cells to separate the electrolysis products. Losses of chlorine and oxidation of magnesium by oxygen of the air are prevented by protecting the cell with a ceramic cover.

Presence of alkali metal chlorides in the melt, potassium and sodium, fails to affect the course of electrolysis, since the decomposition voltage of these salts is higher than that of $MgCl_2$ with the effect that potassium and sodium fail to evolve at the cathode together with magnesium. Presence in the melt even of small amounts of water interferes with electrolysis as cryolite and magnesium chloride tend to hydrolize according to the reaction

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

Magnesium oxide precipitates as slime which is undesirable from the viewpoint of the process. Sulphates tend to affect reduced magnesium in a similar manner

$$Mg + MgSO_4 \rightarrow 2MgO + SO_2 \qquad (217)$$

Trivalent iron is reduced more readily than magnesium and contaminates the latter, while divalent iron oxidizes at the anode, some current being consumed in the process.

It follows then that manufacture of magnesium by electrolysis requires an anhydrous magnesium chloride, one free from residual water, sulphate and iron. Anhydrous magnesium chloride can be obtained by dewatering of natural salts, such as bischofite $MgCl_2 \cdot 6H_2O$ or by chlorination of magnesite and carnallite mixture.

Salts are dewatered by drying and remelting. In order to chlorinate natural $MgCO_3$, it is burned at 700-800°C to caustic magnesite according to reaction (15). Caustic magne-

site is mixed with coal, briquetted and treated by chlorine (16). Manufacture of magnesium chloride from magnesite is more advantageous than dewatering of salts, if use is made of chlorine given off in the electrolysis of carnallite.

To sum up what has been said above, manufacture of magnesium by electrolysis of molten chloride requires the preparation from natural materials of an adequately pure anhydrous magnesium chloride or a mixture of $MgCl_2$ and KCl.

Thermal Techniques for Manufacturing Magnesium

Besides electrolysis, there are other methods for manufacturing magnesium, among them, reduction of magnesium oxide by carbon and other reducing agents at high temperatures, this type of processes being often termed thermal techniques.

A carbon thermal technique is based on the reaction

$$MgO + C \rightleftarrows Mg + CO \qquad (218)$$

Magnesium oxide is mixed with fine petroleum coke and briquetted. Briquettes are heated in hydrogen protective atmosphere at a temperature of about 2500°C. Magnesium evolves as vapours mixed with carbon monoxide.

As the gaseous mixture leaves the furnace, it is rapidly cooled to 120°C by mixing with large amounts of hydrogen or natural gas. A sharp cooling is necessary to quench the gases and thus avoid a reverse reaction, or oxidation of magnesium vapours by carbon monoxide. Magnesium condenses as fine dust, collected from gases in dust catchers and treated by vacuum distillation to yield solid metal.

Carbon thermal technique, requiring complicated and costly equipment, is explosion hazardous as fine dust tends to inflame spontaneously. In modern practice, carbon thermal technique finds few applications.

A silicothermal technique requires lesser temperatures and a simpler equipment. In this technique, magnesium oxide is reduced in vacuum by ferrosilicon, an alloy of iron and silicon, from caustic dolomite, a mixture of CaO and MgO, which suits the technique more than pure magnesium oxide, as calcium oxide promotes reduction.

Caustic dolomite is obtained by burning natural dolomite $CaCO_3 \cdot MgCO_3$ at 1000-1100°C in rotary kilns.

Briquettes from thoroughly mixed caustic dolomite and ferrosilicon powders are heated to 1160-1170°C in air-tight steel retorts by electricity or natural gas.

The following reaction takes place inside the retort

$$2MgO + 2CaO + Si(Fe) \rightarrow Ca_2SiO_4 + 2Mg + Fe \quad (219)$$

Magnesium is removed as vapours, and a residue of calcium silicate and iron remains in the retort. Magnesium vapours are cooled in a condenser to yield a crystalline metal.

This technique is complicated and costly because of a high consumption of retorts. Retorts even from a costly chromium-nickel steel have a short service life. Silicothermal technique is used only, if no deposits of magnesium chloride are available.

55. Manufacture of Anhydrous Magnesium Chloride

Dewatering Carnallite

When heated to 110-120°C, carnallite melts in crystallization water. Dewatering of the melt, whose surface area is less than that of crystals, is slower than that of the crystallized salt, since the rate of vaporization is the greater, the greater the surface area from which the vapours evolve. A higher temperature speeds up drying, but is conducive to hydrolysis

$$KCl \cdot MgCl_2 = KMgCl_3 + H_2O \rightleftarrows KMgOHCl_2 + HCl$$

Oxychloride dissociates readily at temperatures above 550°C

$$KMgOHCl_2 \rightarrow KCl + MgO + HCl \quad (220)$$

Magnesium oxide is objectionable from the viewpoint of electrolysis, while presence of hydrogen chloride in high concentrations in gases brings with it a risk of corrosion of equipment by hydrochloric acid resulting from cooling of gases.

Dewatering is carried out in two steps to increase the capacity of equipment and minimize hydrolysis.

In the first stage, the bulk of water is removed from the solid salt as temperature gradually rises. Carnallite is heated in rotary kilns 25-45 m long, 2.2-4.0 m in diameter, fired by fuel oil or natural gas. The inside surface of the kiln at its hot end, where the temperature is 550-600°C, is lined with refractory brick, and at the cold end, with acid-resistant brick. This prevents corrosion of the steel pipe by gases, carrying hydrogen chloride. The temperature at the raised, or the charging end of the kiln approximates 120°C. As materials move in a countercurrent to the hot combustion gases, their temperature rises gradually to 550°C. The kiln turns out 6 to 7 tons of partly dewatered carnallite, fuel consumption being about 20% in terms of reference fuel. Some 2 to 4% of water remain in the salt. At some plants successful use is being made for the above purpose of fluid-bed reactors whose capacity is much higher than that of kilns.

Second stage of dewatering is carried out in electric furnaces where current is passed through a layer of molten carnallite with the aid of two steel electrodes. A continuous charging maintains a constant level of the melt which is heated to 500°C and flows out as continuously to a holding tank (mixer), heated similarly to the above furnace to a temperature of 750-800°C to ensure adequate settling of magnesium oxide. Two mixers are in alternate operation, while one of them processes the melt, the other is cleaned of residue whose amount attains 10% of the mass of anhydrous chlorides. Salt melt from the mixer is poured into electrolytic cells. The residue is blown with chlorine (a carbon reducing agent is added continuously in the process) in chlorinators where magnesium oxide turns again to $MgCl_2$ that is suitable for electrolysis. Chlorinators are now being also used for the second-stage dewatering of carnallite.

Dewatering Bischofite

This is an even more complicated task, as magnesium chloride hydrolyzes more readily than carnallite. Bischofite $MgCl_2 \cdot 6H_2O$, if dried in the air at usual temperatures, gives off slowly only 5 molecules of water, while the last one can be driven out at temperatures above 240°C only, when hydrolysis proceeds vigorously (220).

Bischofite is dried in rotary kilns in two stages: first, in a current of air at a temperature slowly rising to 200°C, this preventing melting and hydrolysis of the salt, after which a final dewatering is carried out in the presence of coal and some chlorine. The reaction is

$$Cl_2 + H_2O + C = 2HCl + CO \qquad (221)$$

The hydrogen chloride prevents the hydrolysis of the salt.

Besides the use of a corrosion-resistant equipment, operation on bischofite involves a costly vaporization of its natural brine, lake or sea water. For these reasons bischofite is used for the manufacture of magnesium only when no carnallite or magnesite is available.

Manufacture of Magnesium Chloride From Magnesite

Heating of a mixture of magnesite (raw or burned) and coal in a chlorine atmosphere at a temperature of about 1000°C produces molten magnesium chloride by way of the reactions below

$$MgCO_3 + C + Cl_2 \rightarrow MgCl_2 + CO + CO_2 \qquad (222)$$

$$MgO + C + Cl_2 \rightarrow MgCl_2 + CO \qquad (223)$$

A shortcoming of this processing stage is the necessity for a high temperature, and an advantage, utilization of chlorine from electrolysis of $MgCl_2$.

Chlorination of raw natural magnesite is simpler as it requires no burning, but chlorine utilization is low. Whereas burning of magnesite in rotary kilns, which improves chlorine's efficiency, consumes fuel.

Which technique is used depends on the prevailing conditions, but chlorination in both cases is carried out in a practically similar manner in shaft electric furnaces.

The shaft electric furnace is shaped as a vertical cylinder. It is enclosed in a steel casing and lined with refractory brick (Fig. 105). The charge is fed via a hopper in the roof provided with a double air-tight seal. Chlorine is injected through tuyeres at the bottom. The temperature is maintai-

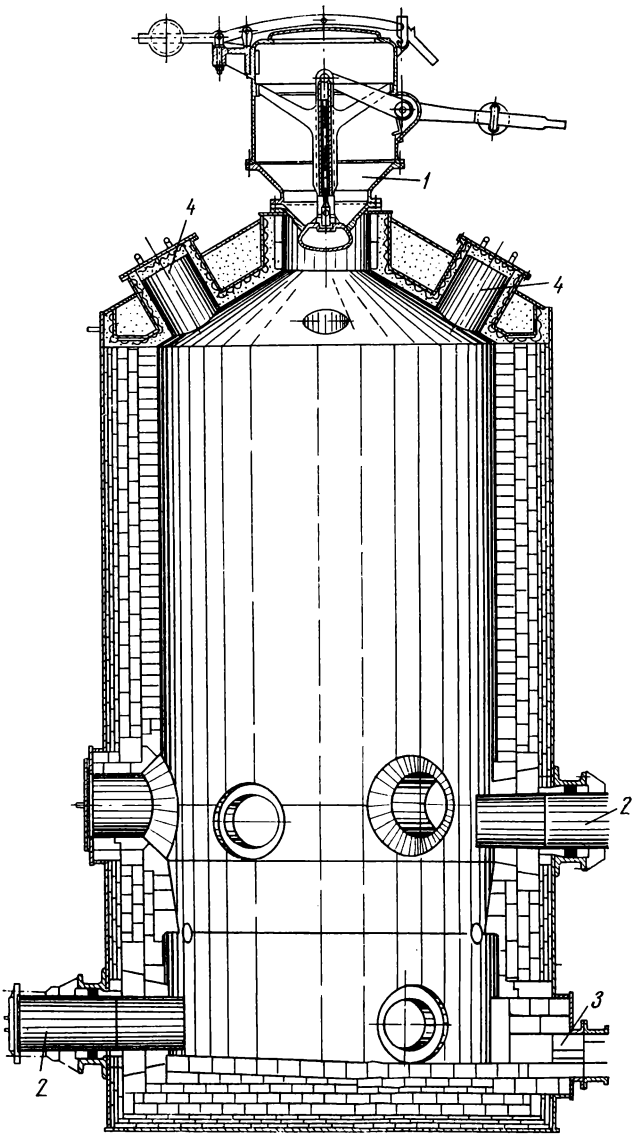

Fig. 105. Shaft furnace for chlorination of magnesite
1—charging hopper; *2*—electrodes; *3*—taphole for discharging melt; *4*—flues

ned chiefly by the heat of chlorination and additionally by electric heating.

Two rows of electrodes of three electrodes per row are placed in the bottom part of the shaft, while the space above the electrodes is filled with a carbon packing. A packing of cylindrical coal briquettes serves as the resistor body, and heat given off in it due to current flow makes it possible to maintain and adjust the temperature of chlorination.

The charge is prepared from natural magnesite and petroleum coke. It is mixed with hot coal pitch and briquetted. In operation on burned magnesite the reducing agent is also petroleum coke, while the binder for briquettes is a small amount of $MgCl_2$ liquor. The MgO and $MgCl_2$ mix hardens to give what is known in construction practice as a magnesian cement.

When charged into the furnace, briquettes fall upon a carbon packing to form a bed which is readily penetrated by chlorine that is supplied from below. Magnesium chloride melts and trickles into the bottom part of the furnace whence it is tapped at regular intervals.

Gases containing CO, CO_2, HCl vapours and other chlorides are removed via a flue in the furnace roof. Gases are neutralized by scrubbing with water and burning, resultant heat being sometimes used as fuel for the furnace.

56. Manufacture of Magnesium by Electrolysis

Composition and Properties of Electrolyte

Anhydrous carnallite contains on the average 49% $MgCl_2$, 42% KCl, 7% NaCl, 1.0% MgO, and 0.1% H_2O. Decomposition voltage of salts making up the carnallite at 700°C is as follows, V: MgCl, 2.6; NaCl, 3.4; KCl, 3.5. It follows then that magnesium settles out at the cathode before sodium and potassium; however, the concentration of $MgCl_2$ drops as electrolysis progresses, while that of NaCl and KCl, rises. The possibility of other cations discharging increases as the electrolyte grows more and more depleted in magnesium. Reduction at the cathode of sodium and potassium simultaneously with that of magnesium is prevented by removing at regular intervals the spent electrolyte (which is enriched

in salts of these metals) and by introducing fresh anhydrous salt in order to maintain a following average composition of the electrolyte, %: $MgCl_2$, 10; KCl, 75; NaCl, 15.

The temperature of electrolysis should be somewhat higher than the melting point of magnesium to allow the latter to float in the electrolyte. Some overheating is also useful in that it lowers the electrical resistance of the melt, its viscosity and voltage across the cell. On the other hand, too high a temperature increases both the losses of magnesium due to vaporization and the consumption of electric power for heating the electrolyte. Account taken of all these factors, the electrolysis is conducted at the temperature interval between 690 and 720°C.

The electrolyte of above composition melts at a temperature of about 550°C. Its depletion in magnesium would have caused poorer fusibility and called for a higher electrolysis temperature, this explaining why $MgCl_2$ content in the electrolyte should be maintained about 8%.

Electric conductivity of electrolyte constituents at 800°C is as follows, $ohm^{-1} \cdot cm^{-1}$:

$MgCl_2$	1.17
KCl	2.42
NaCl	3.57

It follows then that potassium and sodium chloride play a useful part in the electrolyte in that they improve latter's electrical conductivity.

Another major property of the electrolyte is its viscosity, governed chiefly by concentrations of alkali metals, which are almost by three times less viscous than $MgCl_2$. A low viscosity facilitates floating of magnesium cathode droplets in the melt.

Cathodic magnesium is fairly soluble in the electrolyte and tends to give disperse suspensions. Both these phenomena are objectionable because of a possible oxidation of magnesium by chlorine and lowering of current efficiency. Experiments have shown that potassium and sodium chloride cause an appreciable drop in magnesium's solubility and capacity to disperse.

Besides, alkali metal chlorides raise the surface tension of the electrolyte and thus promote coalescence of magnesium

droplets. This is of importance as larger droplets float faster and thus form more readily a surface layer of metal that can be conveniently scooped. Calcium chloride is similar in action to alkali metal chlorides, and, therefore, it is often introduced into the electrolyte.

Small additions of fluorides NaF and CaF_2 promote growth of magnesium droplets at the cathode and so serve the same purpose, but in a different way.

Electrolysis of carnallite alone is disadvantageous because of a high fall of spent electrolyte which is to be removed from the cell. Consumption of carnallite per ton of magnesium attains 10 tons. Spent electrolyte may be used as fertilizer.

It is by far more economically attractive to process carnallite together with magnesium chloride obtainable from magnesite or as a by-product of titanium manufacture. The starting ratio of salts is chosen in a manner to utilize completely all of the chlorine given off in electrolysis for the preparation of anhydrous magnesium chloride or for the manufacture of titanium.

Thus, when carnallite is charged together with magnesium chloride, the electrolyte may be renewed at less frequent intervals as its contamination by impurities slows down.

As the proportion of carnallite is low, use is often made of electrolytes in which KCl (that exerts a favourable action upon electrolysis) is replaced by $CaCl_2$, the electrolyte's composition then being, %: $MgCl_2$, 10; $CaCl_2$, 45; NaCl, 30; KCl, 15.

Reduction Cell Design

In principle of operation, commercial reduction cells correspond to diagram in Fig. 104, but differ in design and power rating. Modern reduction cells are rated for current intensities of 80 000 and 130 000 A.

Cells are set on a foundation and enclosed in a steel casing. The walls and hearth are lined with fireclay brick (Fig. 106). Anodes are assembled of graphite slabs connected at the top by bolts and a common steel overlapping strip and a copper busbar to supply current. Anode enters the cell through a slot in the anode roof made from refractory concrete in the form of an overturned box. Gas-tight membranes from slabs of

dense fireclay are tightly fitted between the longitudinal walls of the box. Chlorine that evolves in the electrolysis is exhausted from the cavity underneath the roof. All clearances of the anode space should be packed with an asbestos braid and grouted with alumina cement.

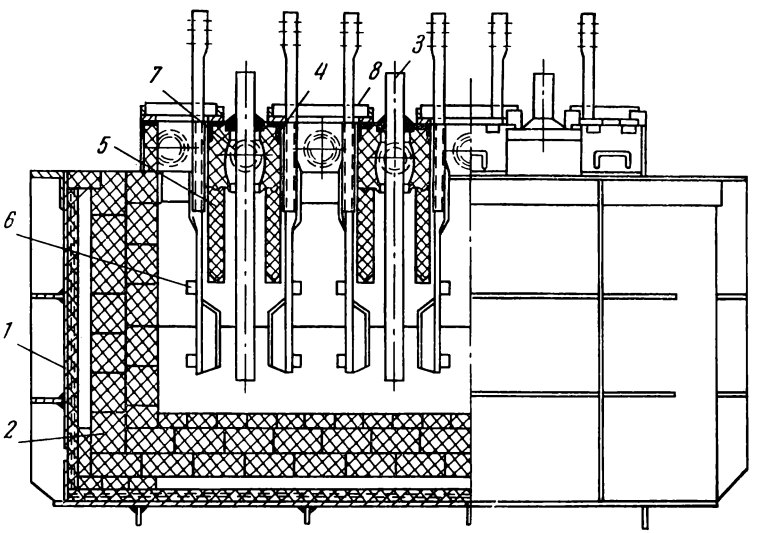

Fig. 106. Cell for electrolysis of magnesium chlorides
1—casing; *2*—fireclay brick lining; *3*—graphite anode; *4*—anode box; *5*—membrane; *6*—cathode; *7*—opening for removal of chlorine; *8*—cathodic space cover

Cathodes are of steel sheets 8-10 mm thick, curving out in the direction of the anode. The sheets are welded to heavy steel bars. Cathodes are perforated to level off electrolyte composition and facilitate floating of magnesium droplets. In the top part of the bath, the cathodic space is closed by fireclay slabs and a gas-tight cover. Two cathodes and an anode make a unit cell, each reduction cell generally comprising four such unit cells connected in parallel.

Reduction cells are connected in a series circuit of 60 to 100 pieces, depending on the voltage rating of the power source available A voltage drop across one reduction cell approximates 6 V, and, therefore, a circuit of a hundred

reduction cells requires a supply voltage of $100 \times 6 = 600$ V.

Service life of reduction cells is 5 to 7 years, continuous operation between overhauls being about a year. Anodes are replaced after 8 to 9 months, cathodes after a few years.

Besides the top-mounted anode cells, there are other types of cells in which anodes are introduced from the sides to simplify current supply and so lower the voltage across a cell by about 0.6 V. Side anodes are by 2-2.5 times more durable, but their replacement is more difficult, as it requires a complete draining of the cell. To date, side anodes are used on a relatively small scale.

Servicing Reduction Cells

Carnallite or magnesium chloride is poured into the cells through cathodic spaces. To this end, molten salts are transported in gas-tight ladles to avoid absorption of atmospheric moisture. Spent electrolyte is removed also via cathodic spaces.

Temperature is adjusted in a number of ways, depending on its variations. If those are less than 40°C, by adjusting suction of chlorine and if the variations are greater than 40°C, by adjusting the concentration of magnesium in the melt. Magnesium lowers the electric conductivity of the melt and thus causes an increase in its temperature, while depletion of the electrolyte in magnesium results in cooling the cell. In case of sudden sharp rise of temperature, the cell is fed with solid salts whose melting consumes much heat.

Magnesium is removed from the cathodic space with the aid of vacuum ladles (Fig. 107). The ladle is transported to a cell by crane, the suction pipe is lowered into the cathodic space, after which a valve is opened. An empty ladle is first preheated to avoid freezing of the metal. As a vacuum builds up inside the ladle, molten magnesium is sucked in together with a small amount of electrolyte. The ladle is filled by moving it from cell to cell, the electrolyte that has separated at the bottom is poured back into cells, and finally the magnesium is cast into moulds.

A deposit containing magnesium oxide resulting from the action of moisture, sulphates and other impurities (as dis-

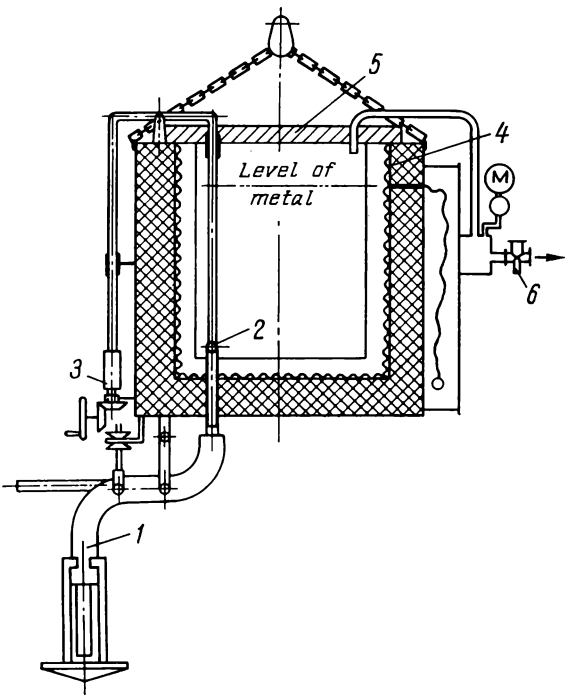

Fig. 107. Vacuum ladle for removal of magnesium from cells
1—suction pipe; *2*, *3*—shut-off valves; *4*—heater; *5*—cover; *6*—connection to source of vacuum

cussed above) tends to accumulate gradually on cell bottom. Slime deposits are removed by a vacuum ladle every 2 or 3 days.

Magnesium Manufacture Performance

One gram-equivalent of magnesium is $\frac{24.32}{2} = 12.16$ gram. According to Faraday law, the deposition of one ton of the metal requires

$$(It)_t = \frac{26.8 \cdot 10^6}{12.6} = 2210 \text{ Ah}$$

Consumption of electric power per ton of magnesium is

$$W = 2210 \frac{v}{K_e} \text{ kWh}^*$$

Average voltage across the cell is 6 V, and the current efficiency, about 85%. Substituting these values, we obtain

$$W = 2210 \frac{6}{0.85} = 15\,600 \text{ kWh/t}^*$$

The manufacture of one ton of magnesium calls for about 4.3 t of anhydrous $MgCl_2$ or 9-9.5 t of anhydrous carnallite.

57. Refining of Magnesium

Settling or Remelting with Fluxes

The USSR State Standard GOST 804-62 specifies one grade of magnesium Mr (99.9% Mg).

Electrolytic magnesium carries up to 5% of various impurities, mechanical ones in their majority which can be removed by simple remelting of the metal with fluxes that prevents its oxidation by the oxygen of the air.

Fluxes are easy-melting mixtures of salts, fluorides and chlorides, whose melts wet magnesium adequately. Chief flux components are generally $MgCl_2$ and KCl with admixtures of $BaCl_2$, NaCl, $CaCl_2$ and CaF_2, as, 45% $MgCl_2$, 40% KCl, 5% $BaCl_2$, 5% $CaCl_2$.

Molten metal from the vacuum ladle is transferred to a crucible furnace heated by gas or electricity to 710-720°C, mixed with fluxes and held there for 10-15 minutes. Nonmetallic inclusions are melted with fluxes and removed with the latter.

Before casting, the crucible is somewhat cooled until a crust of fluxes forms at the surface, the crust is then pierced, and magnesium is cast into cast iron moulds, the crucible being tilted by a special device.

Surface of metal ingots is cleaned of visible contaminations and washed in a bath with hot weak alkali liquor, then in running water. A protective oxide film is formed by immersing ingots into a bath with a hot solution of K_2CrO_4, then dried and coated with fat.

* Conversion to units of the SI system, see page 314.

Volatilization of Magnesium

Electrolytic magnesium, once it is remelted, is generally suitable for use and manufacture of alloys, while some

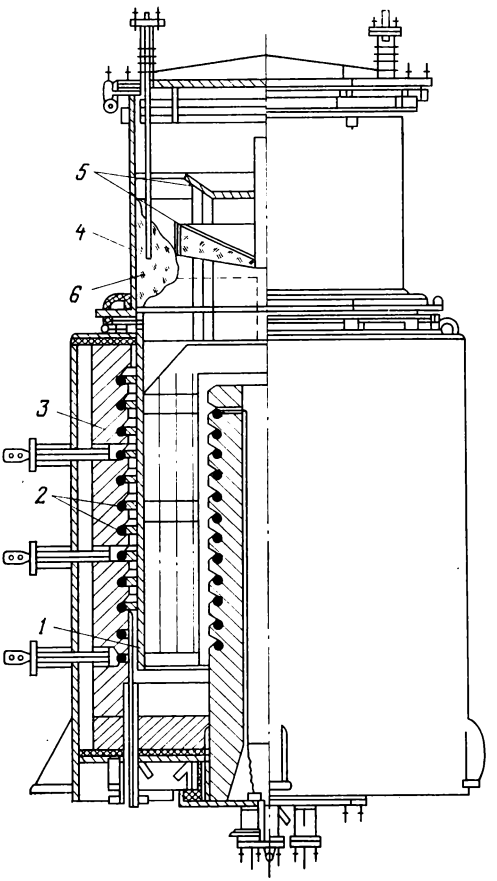

Fig. 108. Vacuum furnace for refining magnesium by volatilization
1—retort (bottom part—vaporizer); *2*—heaters; *3*—lining; *4*—retort (top part—condenser); *5*—shields; *6*—crystals of magnesium

consumers require a purer metal. For such consumers, magnesium is refined by vacuum volatilization.

For a residual pressure of about 13.3 N/m² (0.1 mm Hg), boiling points of magnesium and its characteristic admixtures are as follows:

Metal	Mg	Fe	Si	Al	Ca
Boiling point, °C .	520	1560	1470	1270	700

Magnesium can be cleaned of the majority of impurities by vacuum volatilization. A furnace for this purpose (Fig. 108) is a steel retort heated by electric power to 550-600°C. A residual pressure of 6.67-9.33 N/m² (0.05-0.07 mm Hg) is maintained inside the retort.

Volatilization of 250 kg of magnesium takes 18 hours. Its vapours, as they condense, form druses of crystals which in volatilization of magnesium grade Mr may contain, for example, 0.002% Fe, 0.001% Si, 0.002% Al, 0.004% Cu, Ni, Zn, Mn (aggregate figure).

Review Questions

1. From what raw materials is magnesium chiefly manufactured?
Bischofite, dolomite, carnallite, magnesite.
2. What electrolyte constituents raise its electrical conductivity and decrease its viscosity?
$MgCl_2$, KCl, NaCl, $CaCl_2$.
3. What materials are used in the manufacture of cathodes, anodes, and membranes of magnesium reduction cells?
Fireclay, graphite, refractory concrete, iron.

CHAPTER 9

METALLURGY OF TITANIUM

58. Chemical Properties of Titanium

In appearance titanium resembles steel. It is amenable to polishing and retains lustre for a long time. In the air, titanium is stable to red-hot temperatures, but burns to TiO_2 in oxygen.

Titanium is located in group IV of the periodic table of elements, side by side with typical non-metallic carbon and silicon. At the same time, titanium continues the fourth horizontal series of elements and is at the boundary between an analog of aluminium, scandium, and relatively weakly metallic elements, such as vanadium, chromium and manganese, this explaining the changeable valency and the amphoteric properties of its higher oxide.

In its compounds, titanium is di-, tri- and tetravalent. Compounds of divalent and trivalent titanium are strong reducing agents, and of tetravalent titanium, ones of maximum stability.

Oxidation-reduction potential of titanium, given in Table 3, describes titanium as an active metal which cannot be produced by electrolysis of aqueous solutions.

In the air and in water, metallic titanium is stable for a long time owing to a protective action of the surface oxide film. Titanium decomposes hot water very slowly with an evolution of hydrogen. In the presence of alkalies which dissolve the film, the reaction proceeds at a faster rate.

Titanium's reaction with HCl and H_2SO_4 is weaker than that of iron, and it goes in solution as Ti^{3+}.

Nitric acid oxidizes titanium to a poorly soluble titanic acid $TiO_2 \cdot nH_2O$, where n is a variable number.

Titanium dioxide TiO_2, corresponding in composition to mineral rutile, is a fine white powder, widely used as

paint, titanium white. World output of titanium white exceeds 1 000 000 tons a year.

Titanium white is obtained by heating concentrates and rich ores, containing TiO_2, with concentrated sulphuric acid. A water soluble titanyl-sulphuric acid is formed first

$$TiO_2 + 2H_2SO_4 \rightarrow H_2[TiO(SO_4)_2] + H_2O \quad (224)$$

The acid hydrolyzes, after liquors are cleaned of iron and diluted with hot water

$$H_2[TiO(SO_4)_2] + (n+1)H_2O \rightarrow 2H_2SO_4 + TiO_2 \cdot nH_2O \quad (225)$$

Titanic acid precipitate is filtered and turned to TiO_2 by burning.

Titanium dioxide melts at 1825°C. Besides painting, it is used in ceramic and glass industries for the manufacture of glazes, enamels and refractory glasses, and as a catalyst in some organic syntheses.

Reduction of titanium dioxide by carbon is possible at temperatures above 1800°C, but formed in the process are carbide TiC and nitride TiN, both soluble in titanium and making it brittle. Under these temperatures titanium dissolves much oxygen and hydrogen which also impair its ductility.

Problems involved in the manufacture of titanium free from carbides, nitrides and soluble gases have for a long time held up its commercial use. In the second quarter of this century only was an interest aroused in metallic titanium as a structural material or a base for the manufacture of alloys, after a technique was developed to produce titanium in an adequately pure state. Prior to this, titanium was considered brittle and unsuitable for mechanical working.

59. Raw Materials for Manufacture of Titanium

Titanium's clark is 0.6%. Of a plurality of minerals that contain this element, there are two only of commercial importance: rutile TiO_2 and ilmenite $FeTiO_3$.

Rutile is a stablest natural modification of titanium dioxide, its other varieties, anatase and brookite, occurring very rarely. Natural rutile carries up to 10% iron oxides and other impurities which give it a brown, red or blueish

colour. A fairly simple dressing of rutile ores yields concentrates up to 95% TiO_2. However, these ores are rare and cannot meet the needs of the rapidly developing titanium production.

Ilmenite occurs naturally as placers in combination with magnetite Fe_3O_4 and hematite Fe_2O_3. It forms ores known as titanomagnetites, which carry up to 20% of titanium. Titanomagnetites differ in size of crystals of ilmenite and in character of latter's bonds with iron minerals. Coarsely disseminated ilmenite (grains measuring 0.1-0.2 mm across) can readily be separated from magnetite by magnetic separation which serves as the chief dressing technique. Finely disseminated ilmenite, passing sometimes into solid solutions TiO_2-Fe_3O_4, cannot be isolated by this method.

In degree of attraction by a magnet, minerals can be subdivided into strongly magnetic, fairly magnetic, weakly magnetic and non-magnetic. If the force of attraction of iron is taken for 100 units, its value for strongly magnetic minerals is 3.21 to 40.18 (magnetite Fe_3O_4), for fairly magnetic ones, 0.40 to 1.82 (limonite $2Fe_2O_3 \cdot 3H_2O$, ilmenite, wolframite (Fe, Mn) WO_4 and others) and for weakly magnetic ones, which include the majority of nonferrous metal minerals, below 0.37. This is why magnetic separation is not widely used in nonferrous metallurgy and finds its application chiefly for the separation of iron-bearing minerals. Magnetic separation is also applicable to metal working waste. Mixed waste of nonferrous metals and iron (chips, turnings, scrap) can be sorted by magnetic separation techniques.

Magnetic separators intended for coarse materials are rated for operation in the air. Processing of materials in them is termed dry magnetic separation. Separators for materials finer than 6-8 mm can operate both in the air and in aqueous media, this being known as wet magnetic separation. Wet separation often yields better results as regards finer materials as water prevents sticking together of magnetic and non-magnetic particles.

Magnetic dressing of fine ores and concentrates of nonferrous metals is carried out in magnetic separators of a variety of designs. Among machines most suitable for above the purpose are magnetic separators shown in Fig. 109.

A disk separator used for dry magnetic separation of weakly magnetic ores carries an endless conveyor belt *2* that passes around pulleys *4*, one of which is a driving one. Electromagnets with adjustable magnetic field are placed between strands of the conveyor belt. Rotary iron disks *3*, each similar to an overturned bowl with pointed edges, are fitted above the top strand. Shafts of disks are somewhat

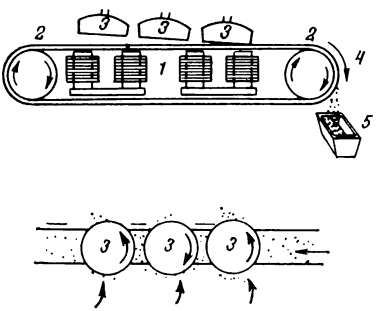

Fig. 109. Disc-type magnetic separator
1—electromagnets; *2*—conveyor belt; *3*—disks; *4*—driving pulley; *5*—receiving hopper for non-magnetic fraction

sloped, and owing to this the right edge of each of them is nearer the belt than the left edge. Because of induction, a magnetic field concentrates at the pointed edges of disks, and its strength on the right-hand side is greater than that on the left-hand side. As they are carried underneath the disks by the moving belt, magnetic minerals are attracted to edges of disks. Diameter of disks is greater than the width of the pole shoe and the belt, and therefore their edges demagnetize at regular intervals as the disks rotate with the effect that lumps of magnetic minerals are dropped into lateral receiving hoppers. Non-magnetic materials are collected in receiving hoppers *5*. Provision of three disks of different magnetic fields and sloping of disk shafts allow to isolate up to six products of different magnetic susceptibilities from the starting material.

Ilmenite is separated from silicates and other relatively light non-magnetic minerals by gravitational methods.

Concentrates may contain up to 50% of TiO_2. Chemical composition of a typical concentrate is as follows, %: TiO_2, 42; FeO, 28; Fe_2O_3, 21; CaO, 1; SiO_2, 2; Al_2O_3, 2.5; MgO, 2.5.

60. Titanium Manufacturing Techniques

Preparation of Titanium Tetrachloride

Treatment of ilmenite pursues the aim of obtaining a chemical concentrate of titanium. If the goal is the manufacture of metallic titanium, the concentrate is $TiCl_4$. Generally, the final product is an aqueous chemical concentrate of TiO_2 which is used as paint.

In application to metallurgy of iron and steel, ilmenite is treated by reduction smelting to yield ferrotitanium containing 18% Ti, 5-8% Al, 3.5-6% Si, 3-4% Cu and up to 1% of other impurities. Reduction smelting of ilmenite concentrate in electric furnaces also produces titanium cast irons and a slag with 70-80% TiO_2 which serves as a starting material for the preparation of titanium tetrachloride.

Slags with such a high content of titanium dioxide are quite viscous. Their manufacture in molten state requires temperatures higher than 1500°C which are practically impossible to attain in a blast furnace hearth. Therefore, the charge is smelted in arc furnaces with a least amount of fluxes.

The charge is composed of an ilmenite concentrate, coke or anthracite in lumps of about 4 mm across. The reducing agent is proportioned in a manner to obtain a slag with some 5% FeO, this objectionable impurity being left in the slag to lower its viscosity.

To lower the consumption of electric power, about a half of the charge is briquetted, and the remainder is charged as powder. Recovery of titanium to slag exceeds 90%, its approximate composition being, %: TiO_2, 76; FeO, 6; SiO_2, 5; Al_2O_3, 2; (CaO + MgO), 4.

Titanium tetrachloride is obtained by chlorination of briquettes from ground slag or rutile concentrate in the presence of coal. At a temperature between 600 and 800°C, the reactions below take place, the first two ones being

particularly intensive

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2 \quad (226)$$

$$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO \quad (227)$$

$$TiO_2 + 4Cl_2 + 2C \rightarrow TiCl_4 + 2COCl_2 \quad (228)$$

Resultant tetrachloride is a gas since its boiling point is 136°C. Preparation of $TiCl_4$ directly from ilmenite by this technique is made difficult because of a side formation of large amounts of $FeCl_3$ which is also volatile (its boiling point is 319°C). Separate condensation of $TiCl_4$ and of $FeCl_3$, when the latter is present in high concentrations, is a problem which makes a direct chlorination of ilmenite inefficient.

Reduction of Titanium Tetrachloride

Titanium tetrachloride is purified by fractional distillation which is described below, then reduced by magnesium according to a reaction that proceeds fairly vigorously even at temperatures between 800 and 900°C

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

Anhydrous $MgCl_2$ — a side product — is suitable for the manufacture of magnesium by electrolysis, chlorine resulting from the electrolysis being utilized in the preparation of $TiCl_4$.

Therefore, it is good practice to combine production of magnesium with that of titanium which supply each other with the necessary components.

$TiCl_4$ is reduced by magnesium at a temperature below the melting point of titanium which is obtained as fritted crystals, or sponge. The bulk of liquid $MgCl_2$ is poured out, while the remaining portion is separated from the sponge by vacuum distillation or leached by water. The sponge is remelted in vacuum or in argon atmosphere.

Titanium may be reduced from its tetrachloride also by sodium

$$TiCl_4 + 4Na \rightarrow Ti + 4NaCl \quad (229)$$

Sodium is cheaper than magnesium and a more efficient reduction agent. Along with these advantages, there are some processing problems which make sodium reduction less profitable today.

Reduction of Titanium Dioxide

Titanium dioxide may be reduced to titanium sponge at a temperature of about 1000°C by the action of calcium or calcium hydride according to reactions

$$TiO_2 + 2Ca \rightarrow Ti + 2CaO$$

$$TiO_2 + 2CaH_2 \rightarrow TiH_2 + 2CaO + H_2$$

Calcium oxide is leached out of the sponge by a dilutee hydrochloric acid. Heating decomposes titanium hydridt to titanium and hydrogen. Both these methods are as yee insufficiently studied. Manufacture of titanium by thesn techniques involves no preparation of and purificatio. of $TiCl_4$, but the starting material (pure TiO_2) is more costly

61. Production of Pure Titanium Tetrachloride

Chlorination of Titanium Dioxide

Ground slag or rutile concentrate is mixed with coal and coal pitch and briquetted. Briquettes are heated without the access of air at a temperature of 800°C. Coking of pitch reinforces briquettes and makes them porous.

Chlorination is carried out in shaft electric furnaces described previously (see Fig. 105).

Above reactions (226-228) result in gases that contain, besides $TiCl_4$ vapours, some $SiCl_4$, an excess of chlorine, CO, CO_2, $FeCl_3$ and other volatile chlorides. Gases are directed from the furnace to a settling chamber, where iron and aluminium chlorides condense and settle together with mechanically entrained dust. Gases then pass through packed towers sprayed with cooled liquid $TiCl_4$. The bulk of volatile chlorides condense inside the towers, the balance being collected in tubular coolers at a temperature minus 10-15°C. Liquid $TiCl_4$ is drained to a thickener where remaining solid particles settle out as waste slime. A proportion of clarified tetrachloride is cooled in a cooler and returned to the spraying towers, the other portion is filtered through porous ceramics or activated carbon and transferred to

further purification. A schematic diagram illustrating the condensation of vapours is given in Fig. 110.

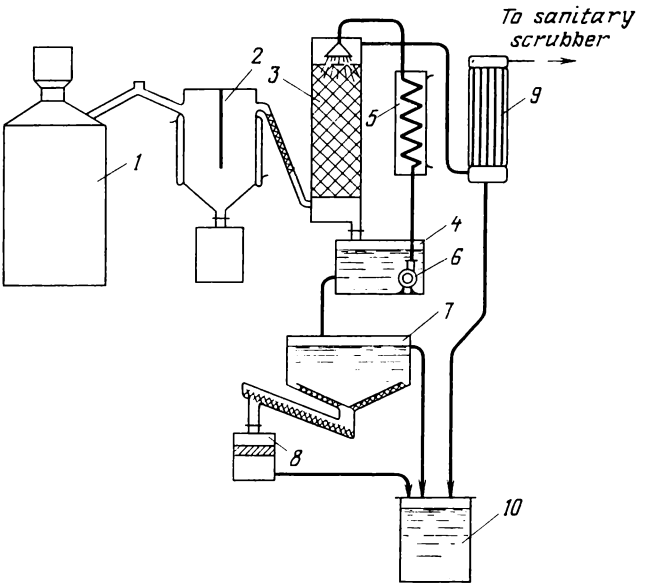

Fig. 110. Condensation of chlorides from chlorination gases
1—blast furnace; *2*—settling chamber and condenser for solid chlorides; *3*—spraying tower; *4*—collector; *5*—cooler; *6*—pump; *7*—thickener; *8*—filter; *9*—condenser; *10*—commercial titanium tetrachloride collector

Commercial titanium tetrachloride has the following approximate composition, %: $TiCl_4$, 99; Si, 0.3; Al, 0.1; Fe, 0.02; V, 0.1; Cl_2, 0.05.

Purification of Titanium Tetrachloride by Fractional Distillation

Commercial $TiCl_4$ is cleaned of impurities by fractional distillation on the basis of different boiling points of chlorides:

Chloride	$TiCl_4$	$FeCl_3$	VCl_4	$VOCl_3$	$SiCl_4$
Boiling point, °C	136	319	164	127	57

Prior to fractional distillation, commercial titanium tetrachloride is passed through copper chips heated to 90-100°C to partly reduce iron and vanadium respectively to Fe^{2+} and V^{4+}, whose chlorides have higher boiling points, and to bind excess elemental chlorine in $CuCl_2$.

Fractional distillation is a technique for separating mixtures of liquid substances based on differences in boiling points of constituents involved. In a vaporization of a mixture, vapours are always enriched in the low-boiling component (LBC). If these vapours are condensed the resulting liquid has an even lower boiling point than the starting one and is richer in the low-boiling component. Therefore, a pure LBC can be condensed from vapours by repeating vaporization and condensation a number of times. The high-boiling component (HBC) concentrates in the distillation residues.

All these operations are performed in a single apparatus known as a fractional distillation column which is assembled of trays (Fig. 111).

A mixture to be separated is fed to a vaporizer heated from outside and vaporizer being located at the bottom of the column where the mixture is in constant boiling. Vapours rise inside the column, give off heat and condense on trays. As a tray is filled to overflow level, the liquid trickles down. These flows are continuous and when all taken together they make up a reflux which carries all the high-boiling components back into the still.

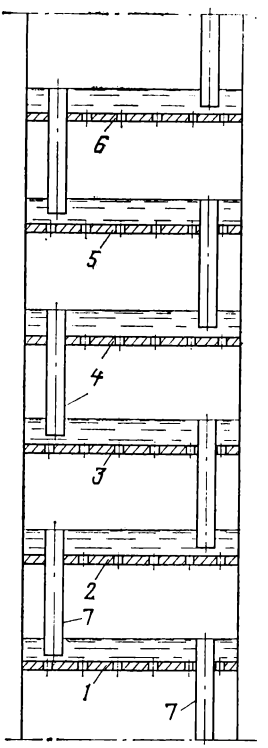

Fig. 111. Fractionating column

1 through *6* — trays; *7* — overflow devices

From bottom up, each successive tray contains a greater amount of LBC in the liquid. A calculation can determine

the number of trays required to obtain a practically pure LBC in vapours from the topmost tray. These vapours are transferred to a condenser, and the condensate is a finished purified product.

Fractional distillation is continued as a batch process until a given amount of still residue accumulates, the resi-

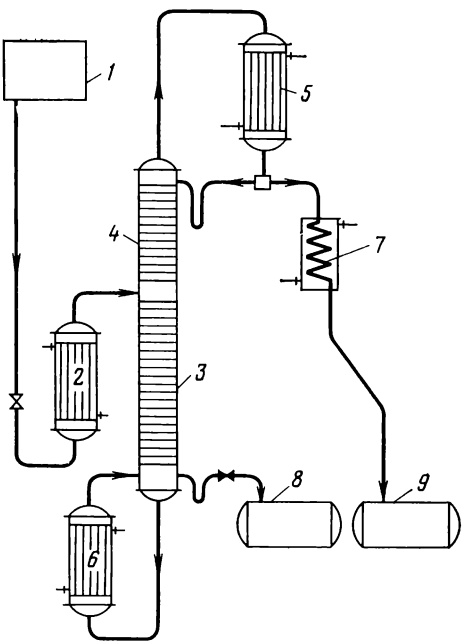

Fig. 112. Continuous fractionating technique

1—head tank; *2*—heater; *3*—extractive section of column; *4*—concentration section of column; *5*—dephlegmator; *6*—still; *7*—cooler for distillate; *8*—still residue collector; *9*—distillate collector

due being then either dumped or treated separately. A continuous fractional distillation, whose flowsheet is shown in Fig. 112, is more productive. The purification technique is essentially the same, but the vaporizer for the LBC is the bottom part of the column, termed the extractive section which is assembled of trays. Rising vapours enter the con-

centration section of the tower, LBC concentrations gradually rising in successive trays. Condensation supplies heat, and, therefore, the liquid boils constantly even on trays of the concentration section of the column. From the column, vapours pass into a dephlegmator, where HBC residue condenses and which produces the bulk of reflux that trickles back into the column.

Fractional distillation (rectification) of $TiCl_4$ is carried out in two steps, in two rectification columns arranged in series. In the first column the commercial product is treated to yield a relatively low-boiling $SiCl_4$ which is a valuable side product, and in the second column, $TiCl_4$ is isolated from even more high-boiling impurities.

Purified $TiCl_4$ should be free from iron, vanadium and silicon (their contents should be kept below 0.01% each).

Recovery of titanium in chlorination of slag is about 90%, and in purification of tetrachloride the recovery may be as high as 95%. Overall recovery from raw materials to purified tetrachloride is $0.9 \times 0.95 \approx 0.85$.

62. Manufacture of Metallic Titanium

Reduction of Titanium Tetrachloride by Magnesium

Reduction is carried out as a batch process in gas-tight retorts of stainless steel filled with argon. Retorts are placed vertically in an electric or a gas fired furnace. From the top, it is closed by a cover with a rubber seal cooled by a local water cooler. The cover is fitted with pipes for charging magnesium, feeding $TiCl_4$, sucking of air and supplying argon. Retort capacity allows the manufacture of up to 1500 kg titanium sponge per operation.

Once a retort is placed inside a furnace, air is sucked out of the retort, and it is filled with argon. Next, liquid magnesium is poured at a temperature of about 700°C, and feeding of liquid titanium tetrachloride is begun. The heater is deenergized and the temperature is maintained in the 800-900°C range by adjusting the rate of $TiCl_4$ feed. A retort may also be cooled on the outside by blowing with air. Removal of heat speeds up reduction.

Liquid magnesium chloride is discharged at regular intervals through a pipe in retort bottom. After a calculated amount of $TiCl_4$ is introduced, and the reaction dies out, heating is switched on and the retort is held for about one hour at 900°C to complete reduction. Next, the retort is removed from the furnace by a crane and cooled with water. Its contents are now titanium sponge, magnesium chloride residues, which have infiltrated sponge pores, and excess amounts of magnesium.

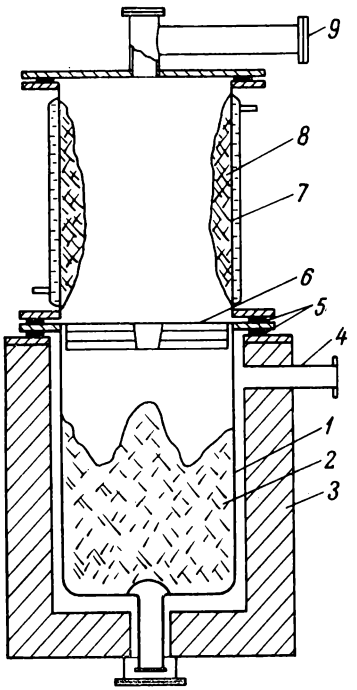

Fig. 113. Separating titanium sponge from $MgCl_2$ and excess magnesium

1—retort; *2*—reaction products; *3*—electric furnace; *4*—pipe for sucking air out of furnace; *5*—rubber gaskets; *6*—shields; *7*—condenser; *8*—condensate; *9*—pipe for sucking gas out of retort

To separate reaction products, use is made of differences in their vapour pressures at 900°C in vacuum. Under these conditions, titanium vapour pressure is negligibly small, that of magnesium chloride, about 1.07 kN/m² (8 mm Hg), and that of metallic magnesium, about 10.7 kN/m² (80 mm Hg).

The cover of the retort is taken off, and a water-cooled condenser is put in its place. The retort is again introduced into the furnace and sealed inside the latter in a manner to allow building of vacuum both inside and outside of the retort (Fig. 113). These precautions are taken to prevent deformation of steel walls by atmospheric pressure. If a vacuum is provided on both sides of walls, no difference in pressure exists, and the hot walls are free of any load. Magnesium and magnesium chloride are distilled at 900°C and residual pressure of the order of $113.3 \cdot 10^{-4}$ N/m² (10^{-4} mm Hg) for 25 hours.

The retort then is cooled, and titanium sponge is knocked out by air-powered chisels. Sponge's chemical composition is as follows, %: H_2, 0.002; O_2, 0.05; N_2, 0.02; Cl, 0.07; Mg, 0.08; C, 0.1; titanium, the balance.

At some plants, distillation is carried out in special retorts into which reduction products are charged in dry premises where air moisture can cause no partial hydrolysis of $MgCl_2$ with the formation of poorly volatile oxychlorides, e.g., Mg(OH)Cl. In this process, retorts are used to fuller capacity, but working in dry premises is difficult.

Melting of Titanium Sponge

Sponge is melted to ingots in an arc furnace of a special design, suited for operation under vacuum conditions which prevent contamination of the titanium by air gases.

The material of the crucible may also contaminate titanium, and, therefore, the sponge is melted in a copper mould with water-cooled walls. As it solidifies against the cold walls, titanium fails to weld together with copper.

Mould bottom or titanium ingot serves as one pole of a DC arc, the other electrode from graphite (carbon) or titanium being lowered into the mould from the top. Titanium electrode melts in the process and is termed consumable. After the arc is struck, arc length is adjusted by means of a solenoid which surrounds the melting space.

Melting of sponge by means of a graphite electrode gives an alloy of titanium somewhat contaminated by a carbide. Resultant metal is, therefore, used for the manufacture of consumable electrodes. Sometimes, consumable electrodes are pressed from sponge to obviate the need for melting them with the use of a graphite electrode. Pressing of large consumable electrodes requires presses of about 3500-ton capacity.

A universal arc furnace for melting titanium with both graphite and consumable electrodes is shown in Fig. 114. It has a device for moving the electrode vertically and lowering the copper mould bottom in order to obtain elongated cylindrical ingots.

Before melting is started, air is sucked out of the melting space to a residual pressure of 6.66 N/m^2 (0.05 mm

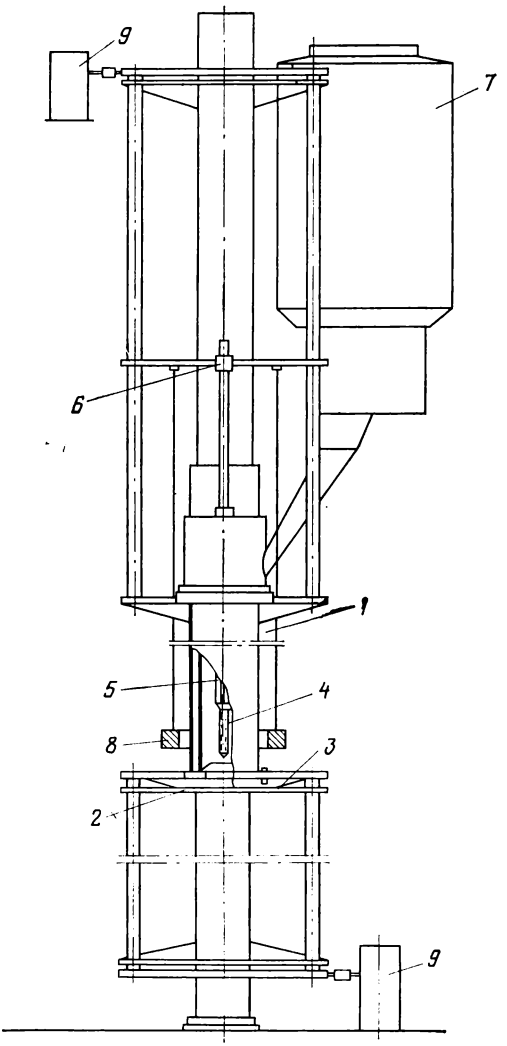

Fig. 114. Arc furnace for melting titanium

1—water-cooled copper mould; *2*—mould bottom plate; *3*—mechanism for lowering bottom plate; *4*—carbon electrode; *5*—electrode holder; *6*—electrode travel mechanism; *7*—sponge hopper; *8*—solenoid; *9*—electric motor gearbox

Hg). The graphite electrode is lowered, an arc is struck and stretched by the solenoid field to 150-200 mm. Sponge and titanium waste (cuttings, shavings) are fed gradually inside the melting space from a hopper. Mould bottom is slowly lowered to produce a titanium ingot of required length. This ingot is welded to a consumable electrode holder instead of the graphite electrode, and the ingot is remelted. In this second melting with the consumable electrode, arc length is about 35 mm, voltage, 30 V, current intensity, up to 5400 A.

To obtain alloys of titanium with aluminium, manganese, vanadium, chromium and other metals, alloying additions are introduced into sponge which is fed to the first melting stage. When the material is remelted, the additives distribute themselves fairly uniformly throughout the body of the ingot.

Manufacture of Extra Pure Titanium

Generally, the purity of titanium from remelting of sponge is 99.6-99.7%. Some consumers require a purer metal one with 99.9% Ti and even higher.

Pure titanium is obtained in small amounts by processing sponge by the iodide technique which makes use of the reversibility of the reaction

$$Ti + 2I_2 \rightleftarrows TiI_4 \qquad (230)$$

At 100-200°C, the reaction proceeds from left to right, and at 1300-1400°C, from right to left.

Sponge and scrap from titanium working are charged into an annular space between wall of retort and molybdenum wire cloth (Fig. 115). Pure titanium wire, 3-4 mm in diameter and about 10 m long, is fixed in a zigzag fashion to molybdenum holders, then the cover is sealed tight and air is sucked out to a residual pressure of $1.33 \cdot 10^{-2}$ — — $1.33 \cdot 10^{-3}$ N/m^2 (10^{-4} to 10^{-5} mm Hg).

The retort is placed in a thermostat heated to 100-200°C, and inside the retort a bulb holding iodine is crushed by a special device. Titanium wire is heated to 1300-1400°C by passing a current through it. Iodine vapours react with sponge and scrap material to give TiI_4 vapours, which

decompose on incandescent wire to crystals of pure titanium, releasing iodine in the process.

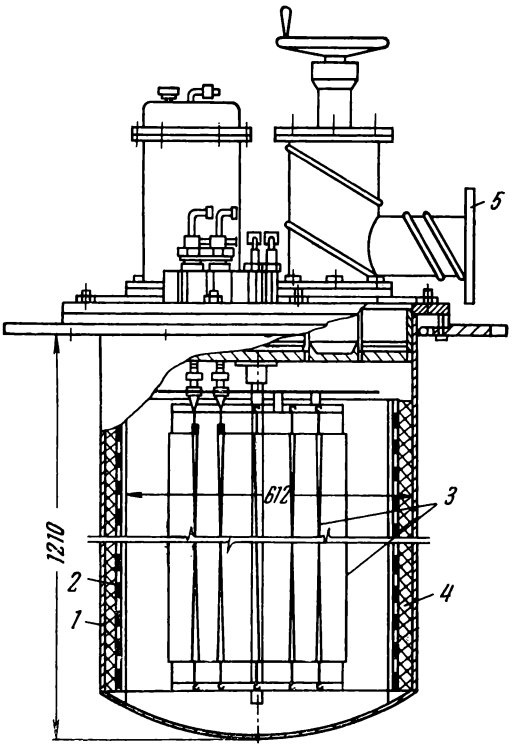

Fig. 115. Apparatus for refining titanium by iodide technique
1—retort wall; *2*—molybdenum wire cloth; *3*—wire of titanium; *4*—titanium sponge; *5*—pipe for connection to vacuum system

The apparatus, shown in Fig. 115, has a productive capacity of some 10 kg of pure titanium per 24 hours.

Review Questions

1. Name chlorides of contaminating elements which are more and less volatile than $TiCl_4$.
$FeCl_3$, $AlCl_3$, $SiCl_4$, VCl_4.
2. What impurities increase hardness and brittleness of titanium?
Fe, Al, N, C, O.
3. What agents are used to reduce titanium from $TiCl_4$ and TiO_2?
Mg, Na, Ca, CaC_2.

PART III

METALLURGY OF REFRACTORY METALS

CHAPTER 10

GENERAL

Refractory metals were formerly considered rare elements, but in the second quarter of this century some of them became essential materials in new engineering applications, and their present-day yearly consumption runs to tens of thousands of tons.

The generally accepted characteristics of refractory metals, high melting points (above 1650°C) and chief use as alloys with iron, allow inclusion into this group of commercial classification of such metals as tungsten, molybdenum, vanadium, zirconium, tantalum, niobium, manganese and chromium (titanium, rhenium)*.

Besides, a growth in consumption for smelting of special steels, refractory metals find an ever increasing use either as pure metals or as bases of alloys. Today this is particularly true of tungsten and molybdenum whose metallurgy is discussed in the present short course.

Tungsten

In appearance, tungsten resembles steel, while its powder is dark greyish. Features of tungsten are a high density, high melting point and hardness.

In tensile strength, tungsten is similar to hardened steel. Mechanical properties of the metal are much dependent on its working, as forging and rolling increase its hardness and strength.

* See note to Table 4.

Pure tungsten is ductile and forgeable when hot, and it can readily be drawn into a wire tenths of a millimeter thick and rolled to thin sheets.

As invented by N. A. Lodygin (1900), tungsten wire still remains a most suitable material for filaments of electric lamps and radio tubes. It should be noted, however, that tungsten can be worked at high temperatures in vacuum or a protective atmosphere only, as it readily oxidizes in the air.

Other applications of pure tungsten are very few, and it finds use chiefly as an additive to alloys. About 50% of tungsten output is consumed in manufacture of special steels, inclusive of rapid steels. Tools of rapid steel, e.g., lathe tools and milling cutters, allow a high-rate machining of metals. Heat evolving in the process fails to affect the hardness and durability of the tools even if they are heated to 650°C. Besides tungsten, rapid steels are alloyed with chromium, nickel, vanadium and cobalt.

Tools from rapid steels opened new possibilities for a sharp increase in machining efficiency.

Even harder than tungsten is its carbide WC, which is but slightly inferior in hardness to diamond and has found a wide application as a base for the manufacture of extra-hard alloys.

Tungsten carbide is a grey non-fusible powder, its alloys being obtainable by a metalloceramic technique, i.e., by pressing a tool from a mixture of carbide and cobalt powders then fritting it in an hydrogen atmosphere at a temperature of about 1400°C. Cobalt serves as a binding material, its content in the alloy lying between 5 and 15%. In some instances, carbides of titanium, tantalum, niobium are introduced into the above alloys.

In terms of tungsten carbide rating, tools retain their machining properties up to temperatures of about 1100°C. Tungsten carbide alloys are used in the manufacture of lathe tools, drills, milling cutters, drill bits and dies for drawing of wire.

Alloys of tungsten, cobalt and chromium, stellites, containing, %: W, 3-15; Cr, 25-35; Co, 45-65; and C, 0.5-2.7, are not only hard, but heat-, wear- and corrosion-resistant as well. Stellites are welded by electric arc upon critical

working parts of machines, as aircraft engine valves, dies, turbine blades, excavator bucket teeth.

Tungsten and tungsten-cobalt steels possess high magnetic properties and are used in the manufacture of permanent magnets.

Metalloceramic alloys of tungsten with copper and silver combine a high electric conductivity with durability; they are suitable for contact tips that are rated for frequent breaking-and-making and, therefore, suffer from a particularly severe arcing, i.e., working parts of breakers, switches, telegraph apparatus, relays and other similar devices.

Molybdenum

In appearance and high mechanical properties, molybdenum is similar to tungsten. It is also fairly hard and strong with respect to tensile stresses. Electric and heat conductivities of molybdenum are somewhat lower than those of tungsten. When heated without access of air, molybdenum is readily amenable to mechanical working and can be drawn into a thin wire.

Molybdenum retains strength up to temperatures of about 1000°C. It goes to make parts of vacuum apparatus, e.g., hooks for filaments in electric bulbs, targets of X-ray tubes, heaters of high-temperature furnaces, plates of generator and rectifier tubes.

Molybdenum steels, which consume some 90% of molybdenum output, feature a high mechanical strength, wearability and impact strength. Of particular value is the heat resistance of molybdenum steels which is greater than that of tungsten steels for equal amounts of alloying elements. Molybdenum may replace tungsten in rapid steels. Steels alloyed with molybdenum are used in the manufacture of armour and arms, and are generally known as armour, gun and small arms steels.

Molybdenum enters the composition of acid and heat resistant steels in combination with nickel, cobalt and chromium.

Pure molybdenum and molybdenum-based alloys retain strength at high temperatures and serve for the manufacture of parts of jet engines and rockets.

Metalloceramic hard alloys based on molybdenum carbide Mo_2C in combination with titanium carbide TiC, bound with nickel and chromium, are similar to alloys of tungsten carbide, but are less widely used in engineering applications.

Review Questions

1. What refractory metals enter the composition of rapid and magnetic steels?

Zr, V, Mo, W, Nb, Ta.

2. What material is used to make filaments of electric lamps and suspensions for these filaments?

Mo, W.

3. What refractory metals find use in the manufacture of armour, gun and small arms steels?

W, Mo.

CHAPTER 11

METALLURGY OF TUNGSTEN

63. Chemical Properties of Tungsten

Tungsten is a transitional element of period VI and is located in group VI, B of the periodic table. Maximum positive valency of tungsten is six, and it is a stablest valency. Along with this, the outside shell of the atom carries two electrons which provide the lowest valency of 2. Tungsten is less metallic than molybdenum and chrome.

Natural element of atomic mass of 183.86 consists of five isotopes: W^{180}, W^{182}, W^{183}, W^{184}, W^{186}.

In elemental state, tungsten was obtained for the first time in 1783 by I.I. and F. de Elhuyar brothers, while its commercial use dates from the 20th century only, when the effect of tungsten additions on the properties of steel was discovered.

Because of a very high boiling point, tungsten is practically non-volatile which explains its suitableness for the manufacture of filaments of incandescent lamps and radio tubes. Tungsten possesses no reversible electrochemical potential in aqueous solutions because the ion of lower valency is unstable and decomposes water. Tungsten even fails to interact with concentrated strong acids; a mixture of HNO_3 and HF only dissolves it through formation of a complex.

In the air, tungsten oxidizes appreciably when red hot, while if in powder form, it is pyrophoric, i.e., capable of inflaming spontaneously.

The stablest higher oxide WO_3, known as tungsten anhydride (trioxide), possesses acid properties. With water, the trioxide gives a poorly soluble tungstic acid H_2WO_4, which is yellow fine crystalline substance, readily soluble in alkalis and ammonia with the formation of salts, tungstates, e.g., Na_2WO_4, $(NH_4)_2WO_4$ and others. Tungstates

of alkali-earth, heavy nonferrous metals and iron, in particular $CaWO_4$, $FeWO_4$ and others, are insoluble in water.

In alkali liquors, ions of tungstate WO_4^{2-} and of molybdate MoO_4^{2-} give a series of salts, of which ones formed by alkali metals and ammonia are very soluble in water. If an acid is added at a slow rate, both polymerize to isopolyanions which also give, within a narrow range of pH, soluble compounds described by a general formula

$$Me_2^I O.n.RO_3 \cdot mH_2O (R = W = Mo)$$

Of the tungsten isopolyanions, a most characteristic one is $HW_6O_2^{-5}$, while of molybdenum isopolyanions, $Mo_7O_{24}^{6-}$, termed paramolybdate.

If cold tungstate solutions are rapidly acidified by diluted strong acids, the effect is a whitish colloid deposit of $WO_3 \cdot nH_2O$ which turns, when boiled, to a crystalline yellow tungstic acid $H_2WO_4 \cdot H_2O$. The same result is obtained directly by pouring a hot solution of tungstate into a concentrated hydrochloric acid which has been conditioned with HNO_3 to prevent a partial reduction of hexavalent W to pentavalent W by ions of chlorine

$$Na_2WO_4 + 2HCl + H_2O \rightarrow H_2WO_4 \cdot H_2O + 2NaCl \quad (231)$$

Tungsten trioxide may be reduced to metal by carbon at 750°C by way of reaction (8).

Resultant metal is a grey powder contaminated by carbides WC and W_2C. Tungsten is reducible by hydrogen as easily, but without the side formation of other compounds.

Also known are sulphides WS_2 and WS_3, which may be synthesized. However, tungsten's affinity for sulphur is less than that for oxygen, and, therefore, its sulphides are unstable in the air and tend to hydrolize in water, e.g.,

$$WS_3 + 4H_2O \rightarrow H_2WO_4 + 3H_2S \quad (232)$$

WS_3 and MoS_3 react with alkali metals to give water-soluble oxythiosalts of the type $Me_2^I RS_nO_{4-n}$. For tungsten, if n is assumed equal to 4, we have

$$WS_3 + Na_2S \rightarrow Na_2WS_4 \quad (233)$$

64. Raw Materials for Manufacture of Tungsten

Of commercial importance are two minerals: wolframite, an isomorphic mixture of iron and manganese tungstates ($x\mathrm{FeWO_4}\cdot y\mathrm{MnWO_4}$) and scheelite, a calcium tungstate $\mathrm{CaWO_4}$.

Wolframite ores contain up to 1-1.5%, more often 0.3-0.5% $\mathrm{WO_3}$. They occur as veins in quartzites or at the interface of granites and limestones. When parent rocks are weathered, the effect is placers of tungsten ores.

Tungsten associates in ores with tin as cassiterite and with minerals of molybdenum, bismuth, arsenic and copper. The bulk of barren rock is quartz.

Wolframite ores are dressed by gravity concentration and magnetic separation, and scheelite ores, by flotation.

Gravity Concentration

Gravity concentration is based on differences in settling rates in a pulp of solid mineral particles having different densities. For example, density of wolframite ranges from 7.1 to 7.9, and that of quartz is 2.6. It is self-evident then that for same or close size, particles of the former settle more rapidly in water.

A particle settling in a viscous medium, in particular, in water, is acted upon by forces of weight and friction. As a particle begins to settle, it moves at an accelerating rate, but an increase in settling rate is paralleled by that of friction with the effect that after a given time the particle acquires a constant velocity, known as a terminal velocity.

Jigging is deposition from a pulp on tank bottom of particles of minerals in layers corresponding to their densities. Distribution by layers will be the more clearcut, the closer the particles are in size, as, after screening or classification. The need for this latter operation may be obviated when small settling heights are involved and particles fail to attain terminal velocity. The settling velocity then depends chiefly on density value. To limit settling height and avoid capture of particles by one another, jig-

ging is carried out in a pulsating stream of liquid which may be directed either alternately up and down or up only.

A jig is a tank filled with a liquid and fitted with a metal screen set below the surface of the liquid. Pulsations are produced either by the motion of the liquid or by that of the screen. Most extensively used are jigs operating on the principle of a pulsating liquid, the two chief subdivisions of this type of jig being plunger and pulsator varieties.

A plunger jig (Fig. 116) is composed of compartments each of which, in its turn, is divided by a shallow partition into the plunger and the screen compartments. The former houses a plunger *1* actuated from an eccentric *2*, and the latter, a fixed screen. The jig is composed of a series of compartments the screen in each of them being set at a height about 100 mm lower than that of the preceding one.

Each screen carries a bed of crushed magnetite or fine metallic balls. Material of the bed should have a density intermediate between densities of minerals to be separated. Coarse size fractions (8-10 mm) can be jigged without a bed.

An ore pulp is fed to the first compartment and, having passed in succession all the other ones, is drained into launder *7*. Action of plungers that effect 100-300 strokes per minute at an amplitude of 0.5-8 cm produces a pulsating stream of water inside the bed pores. In the process, the rapidly settling heavy grains of minerals collect in the bottom part of cell *4*, and are discharged at regular intervals. Lighter grains of minerals are entrained by the horizontal stream of pulp. Capacity of this type of jigs is 10-40 t of ore per 24 hours per sq. metre of screen area.

A pulsating jig is shown in Fig. 117. A feature of this type of jig is a pulsator which is diagrammatically represented on the right-hand portion of the said illustration. Water enters the pulsator via pipe *3* and passes underneath a rubber membrane *4*, overcomes the load of spring *5*, depresses valve *6* and penetrates the jig, the valve then closing again because of an instant drop in pressure. This results in a directional pulsating stream of water in which minerals are jigged. Frequency of pulsations may be as high as 600 per minute.

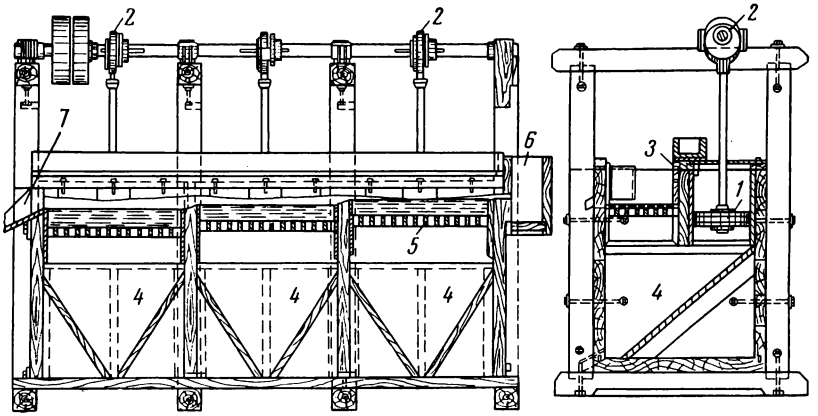

Fig. 116. Plunger jig

1—plunger; *2*—eccentric; *3*—partition; *4*—cell; *5*—screen; *6*—charging box; *7*—launder

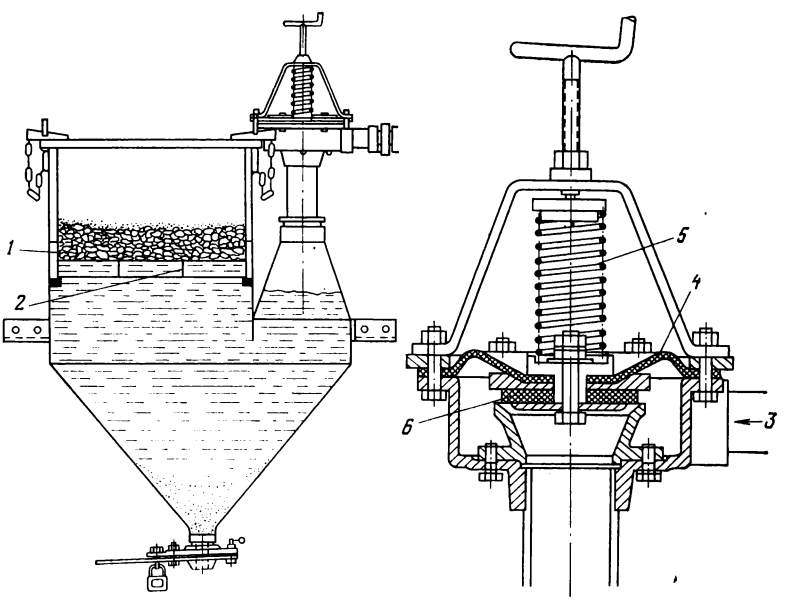

Fig. 117. Pulsator jig

1—bed; *2*—screen *3*—water supply pipe; *4*—membrane; *5*—spring; *6*—valve

Advantages of pulsating jigs are high jigging performance against small consumption of electric power and absence of mechanical drives.

High-frequency jigs operate at 1500-2000 and sometimes even 3000-4000 pulses per minute. Combined high-frequency jigs combine action of piston with vibration of screen. Their performance is particularly good in dressing of slime (fine) fractions of ores.

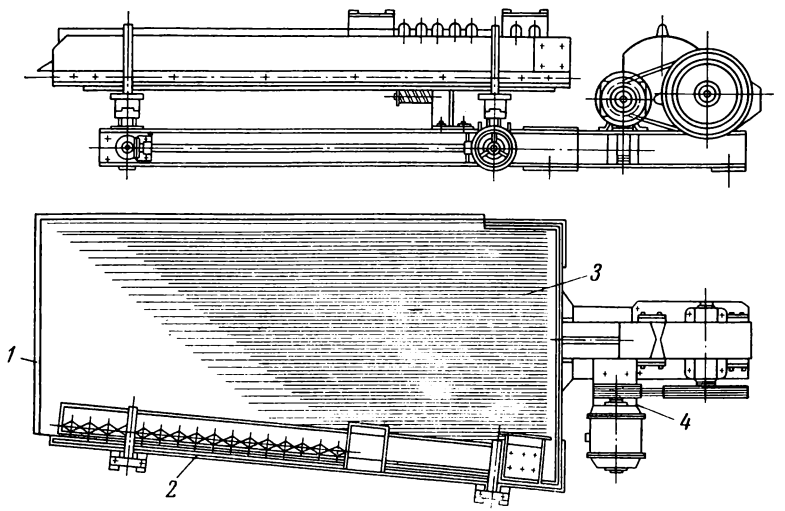

Fig. 118. Concentrating table
1—deck; *2*—charging box; *3*—riffles; *4*—shaker

Gravity concentration may also be effected with the aid of concentrating tables (Fig. 118), whose working surface, deck, is covered with linoleum, canvas, rubber or cement. In addition, decks are provided with a riffling of wooden cleats. The deck is set on a frame at a transverse slope of 9 degrees from the horizontal.

An ore pulp with particles of approximately the same size is fed to a charging box and flows out in a flat stream on the table.

A special mechanism reciprocates the deck in a longitudinal direction in jerks of an amplitude of 12-30 mm at

a frequency of 230-300 times a minute. In the process each and every particle suffers the action of the stream of water which tends to entrain it crosswise with respect to the deck and the action of jerks which tend to carry it in the longitudinal axis of the table. The net effect is that particles move at a given angle with respect to diagonal of the deck, and the ore spreads out fan-wire on the table. Minerals of different densities come off the table at different points, the heavier ones, nearer to the right, the lighter ones, nearer to the left.

Table Flotation

Often a difference in densities of minerals is insufficient to ensure their sharp separation on tables, particularly in sizes less than 2 mm. For this reason, pyrite and other heavy nonferrous metal sulphides are difficult to isolate from wolframite and scheelite. Additions to pulp of collectors, e.g., xanthates and oils, cause flotation of sulphides with the effect that the sulphides float in the stream of pulp on the table and are carried away by the flow.

Flowsheets for dressing tungsten ores are most diversified and complicated, and often combine gravity concentration with magnetic separation, table flotation and customary flotation.

Scheelite can readily be floated with the use of oleic acid as collector, while calcium minerals, calcite and fluorite CaF_2, are prevented from floating by a depressor solution of liquid glass, Na_2SiO_3.

Dressing techniques are variously combined to yield concentrates up to 65-72% WO_3 at a recovery attaining 82-85%.

Given below are customary contents of tungsten concentrates, %: WO_3, 40-70; MnO, 0.008-18.0; SiO_2, 5-10; Mo, 0.008-0.25; S, 0.5-4; Sn, 0.03-1.5; As, 0.01-0.05; P, 0.01-0.11; Cu, 0.1-0.22.

Impurities are additionally removed in some instances by roasting or treating concentrates with acids. Roasting eliminates sulphur and arsenic, and acid treatment, iron and other elements. Acid treatment is also used to remove surface iron oxide films off non-magnetic minerals and prior to magnetic separation.

65. Techniques for Processing Tungsten Concentrates

There are many techniques for processing wolframite and scheelite concentrates, but in either case the first step is to liberate the useful minerals, i.e., to transfer tungsten minerals into readily soluble chemical compounds.

Wolframite concentrates are liberated by sintering or by fusion with soda, the following reactions taking place

$$\left.\begin{aligned} 4FeWO_4 + 4Na_2CO_3 + O_2 &\rightarrow 4Na_2WO_4 + 2Fe_2O_3 + 4CO_2 \\ 6MnWO_4 + 6Na_2CO_3 + O_2 &\rightarrow 6Na_2WO_4 + 2Mn_3O_4 + 6CO_2 \end{aligned}\right\} \quad (234)$$

Scheelite concentrates are broken down in a different manner. Fusion with soda can transfer scheelite to sodium tungstate, but in leaching calcium tungstate is formed again as a deposit

$$CaWO_4 + Na_2CO_3 \rightarrow CaO + Na_2WO_4 + CO_2 \quad (235)$$

$$Na_2WO_4 + Ca(OH)_2 \rightarrow 2NaOH + \downarrow CaWO_4 \quad (236)$$

and, therefore, fusion of scheelite with soda only results in a poor transfer of tungsten to liquor. In plant practice, scheelite is fused with a mixture of soda and quartz sand, calcium forming a poorly soluble silicate

$$2CaWO_4 + 2Na_2CO_3 + SiO_2 \rightarrow Ca_2SiO_4 + 2Na_2WO_4 + 2CO_2 \quad (237)$$

Fused mass or sinter is leached by water, and non-soluble barren rock is filtered off.

Na_2WO_4 liquors are cleaned of impurities, e.g., silicic acid which is present as Na_2SiO_3, arsenic, phosphorus and molybdenum.

Tungstic acid is then settled out (232).

Commercial tungstic acid deposit requires additional purification by dissolving it in aqueous ammonia and re-precipitating it. H_2WO_4 dissolves in ammonia with the formation of ammonia tungstate

$$H_2WO_4 + 2NH_4OH \rightarrow (NH_4)_2WO_4 + 2H_2O$$

then precipitated by hydrochloric acid in the same manner as from a Na_2WO_4 liquor.

A greater purification effect is obtained by causing precipitation of large crystals of ammonia paratungstate

$(NH_4)_{10}W_{12}O_{41}\cdot 11H_2O$, whose formation is the effect of careful addition of acid to the liquor $(NH_4)_2WO_4$ or a partial removal of ammonia by vaporization. Solubility of ammonium paratungstate in water at 70°C is 79.4 gram/litre, and at 17°C, 0.64 gram/litre. Coarser crystals can be obtained by a slow cooling of liquors. Remaining tungstate is separated from mother liquors as $CaWO_4$ and returned to the preceding processing stages (240).

When liquors from leaching of fused mass (alloys) are highly contaminated, it is good practice to settle out H_2WO_4 through formation of calcium tungstate by additions of calcium chloride or lime milk. The reaction is carried out in a boiling liquor (pH = 12-13) agitated by a mechanical stirrer. The residue, after it is treated by repeated decantation by hot water, is a paste which is decomposed by hot hydrochloric acid while stirring and heating it with live steam.

All this may be described by two successive reactions

$$Na_2WO_4 + CaCl_2 \rightarrow 2NaCl + \downarrow CaWO_4 \quad (238)$$

$$CaWO_4 + 2HCl \rightarrow CaCl_2 + \downarrow H_2WO_4 \quad (239)$$

Variants of flowsheets for processing concentrates are given in Fig. 119.

As regards a number of consumers, tungstic acid or ammonium paratungstate is a final product. In other instances, these substances are burned in muffle electric furnaces at 500-800°C to tungsten trioxide

$$H_2WO_4 \rightarrow WO_3 + H_2O \quad (240)$$

$$(NH_4)_{10}W_{12}O_{41}\cdot H_2O \rightarrow 10NH_3 + 6H_2O + 12WO_3 \quad (241)$$

Tungsten trioxide may either be a final product or used for the manufacture of tungsten powder.

If tungsten powder is intended for alloying steels, and presence of carbides in it is admissible, reduction is carried out by carbon. When a manufacture of forgeable ductile tungsten bar, wire or sheet is contemplated, WO_3 should be reduced by hydrogen only.

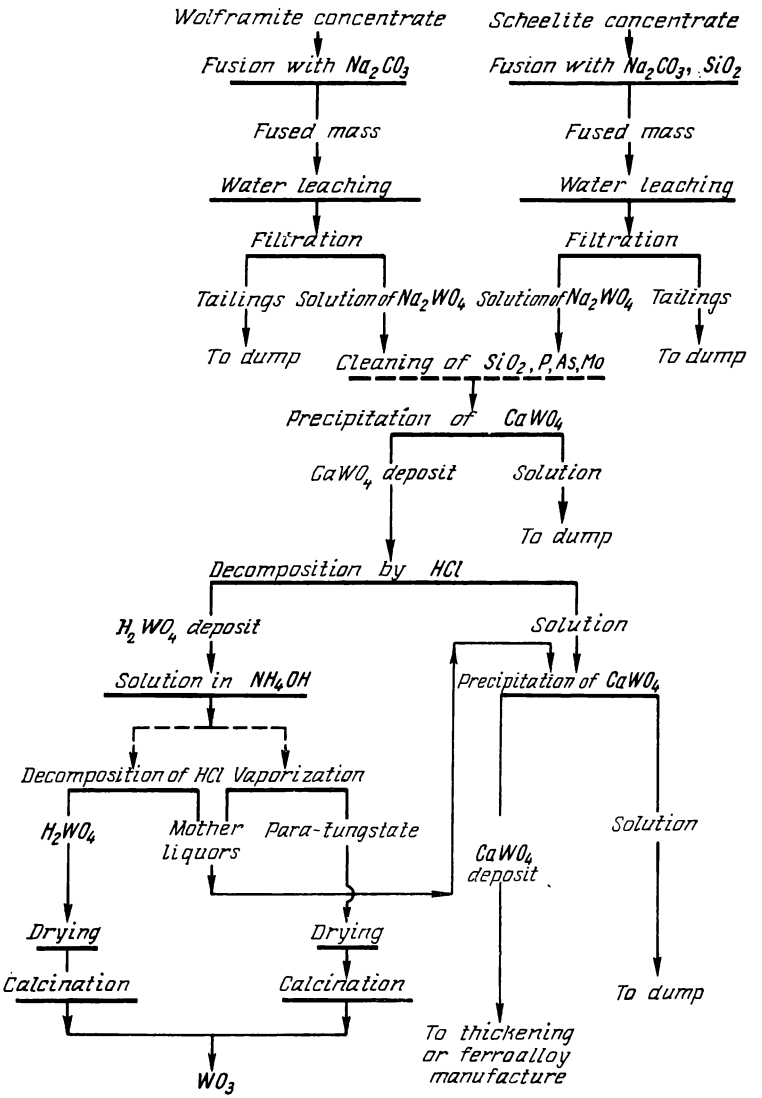

Fig. 119. Treatment of wolframite concentrates after sintering or fusion

66. Manufacture of Tungsten Trioxide

Calcining and Leaching

Calcining is carried out at 800-850°C, and fusion, at 900-1000°C. In this latter process, the access of air to the charge is imperfect, and, therefore, saltpeter is used as an additional oxidizer.

Calcining or fusion of concentrates with soda in small-scale manufactures is conducted in reverberatory furnaces, fired by fuel oil or gas. The charge is made up of concentrate, soda (taken with a 10-15% excess against the stoichiometric amounts), and, if need be, some saltpeter. The alloy is tapped from the furnace, while the calcine is generally rabbled out. When large amounts of raw materials are involved, a continuous calcining technique in rotary kilns is used.

Rotary kilns, similar in design to those for fusing bauxites or calcining alumina, are up to 20 m long and about 2 m in diameter. Their productive capacity may be as high as 25 t per 24 hours.

After grinding, calcine or alloy are leached countercurrently by water in tanks fitted with mechanical stirrers at a temperature between 70 and 90°C, the process yielding Na_2WO_4 liquors with 200 to 270 gram/litre WO_3.

Insoluble residue is separated by filtering or continuous countercurrent decantation in a system of settling tanks. Pulps of a high liquid-to-solids ratio can be advantageously treated in pressure filters described in the chapter dealing with metallurgy of zinc, while thicker pulps are best filtered in vacuum filters. Tailings are scavenged until the content of water-soluble tungsten is brought down to below 0.02-0.03%. Tailings high in tungsten are recycled.

At larger plants that practise continuous calcining, resultant calcine is ground and leached in steamheated drum leaching apparatus similar in design to rod mills.

In application to lean and low-grade scheelite concentrates, V. S. Syrokomski and I. N. Maslenitski have developed a technique for direct leaching in autoclaves by a soda liquor. This requires a temperature of 180-200°C attained at an absolute pressure of about 1.5 MN/m^2 (15 atm). A 3- to

4-fold excess of soda against the stoichiometric amount allows to transfer to liquor of up to 98% of tungsten.

Horizontal autoclaves involved operate on a batch basis. After leaching, pulp is directed to a steam separator (Fig. 88),

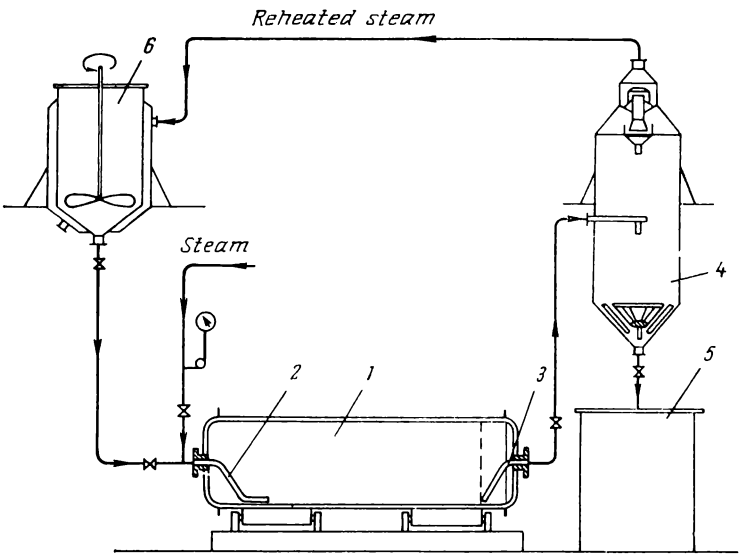

Fig. 120. Autoclave installation for treatment of scheelite concentrates
1—horizontal autoclave; *2*—pipe for supplying pulp and steam; *3*—discharge pipe; *4*—steam separator; *5*—tank for leached pulp; *6*—stirrer for preparation of starting pulp

where the evolving used steam is utilized to heat pulp. A schematic diagram of an autoclave installation is shown in Fig. 120.

Purification of Liquors

Silicic acid, present in liquors as sodium silicate is removed by acidifying liquors little by little with hydrochloric acid or additions of NH_4Cl to pH = 8 to 9. Sodium silicate hydrolyzes to give off a colloid silicic acid which, when

heated and stirred, coalesces and settles out:

$$\begin{array}{l} Na_2SiO_3 + 2H_2O \rightleftarrows 2NaOH + H_2SiO_3 \\ 2NaOH + 2HCl \rightarrow 2NaCl + 2H_2O \\ \hline Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3 \end{array} \qquad (242)$$

Removal of arsenic and phosphorus is based on the formation of poorly soluble magnesian salts of arsenic and phosphoric acids. Prior to settling, arsenites are oxidized to arsenate by sodium hypochlorite

$$AsO_3^{3-} + NaOCl \rightarrow AsO_4^{3-} + NaCl \qquad (243)$$

Magnesium chloride is then added to the liquor, and after boiling for 3-4 hours a residue, composed of $Mg_3(PO_4)_2$ and $Mg_3(AsO_4)_2$, is filtered.

A more complete purification is obtained by introducing ammonia or ammonium salts into the liquor. This results, after an adequately prolonged holding, in a settling of even more less soluble double salts of magnesium and ammonium $MgNH_4PO_4$ and $MgNH_4AsO_4$.

Removal of molybdenum is based on that sodium sulphide reacts first with molybdenum, in preference to tungsten, to bind the former in a soluble oxythiosalt (233). The liquor is then acidified by hydrochloric acid with the effect that molybdenum settles out as MoS_3.

Loss of tungsten is avoided by an accurate proportioning of sodium sulphide.

Precipitation of Tungstic Acid

An acidification of a sodium tungstate liquor causes a yellow deposit of tungstic acid to settle out.

A readily filtered residue is obtained, if the sodium tungstate liquor is poured into a boiling hydrochloric acid that contains a small amount of nitric acid or saltpeter. Nitric acid prevents partial reduction of tungsten to pentavalent tungsten which under the above conditions tends to give blue-coloured soluble compounds.

The acid is settled in rubberized or acid-resistant-tile-lined mechanical agitators. The deposit is scrubbed 6 to

8 times by decantation. An addition of hydrochloric acid or ammonium chloride to scrubbing water speeds up settling and prevents formation of a colloid tungstic acid.

The deposit is 6 to 8 times thoroughly washed with hot distilled water with about 1% of HCl or NH_4Cl, filtered and dewatered in a centrifuge.

In an alternative technique, sodium tungstate is neutralized by hydrochloric acid to an alkali content of 0.3-0.7%, then boiled together with a concentrated $CaCl_2$ liquor. Resultant precipitate of $CaWO_4$, or "artificial scheelite", is contaminated by such impurities as $CaSO_4$ and other insoluble calcium salts, Ca_2SiO_4, $Ca_3(PO_4)_2$ and others. A considerable proportion of deposited $CaSO_4$ dissolves when the precipitate is washed by hot water. Once washed, the pasty deposit is treated by hot concentrated hydrochloric acid with an admixture of HNO_3. This turns artificial scheelite into tungstic acid (239) and causes other calcium salts to go in solution.

$CaWO_4$ is settled out in steel tanks fitted with stirrers, and subsequently decomposed in similar tanks protected by rubber or ceramic tiles.

Purification of Commercial Tungstic Acid

Commercial tungstic acid contains 0.3-0.4% of impurities, chiefly SiO_2, sodium and calcium.

The acid is mixed with water and as a pulp of a liquid-to-solids ratio of 1.5, heated to 85°C, is poured into an ammonia liquor while stirring the latter. After a settling, the $(NH_4)_2WO_4$ liquor with about 300 gram/litre WO_3 is poured off, and the deposit is washed by decantation.

To effect the settling of a fresh portion of pure H_2WO_4, a hot liquor of ammonium tungstate is poured into boiling hydrochloric acid while stirring the lot. Purification is improved by repeating dissolution and settling.

A purer product is obtained by settling ammonium paratungstate from $(NH_4)_2WO_4$ liquors. In this technique, a hot ammonia liquor is vaporized in stainless steel apparatus and crystallized. As a proportion of ammonia is lost with water vapours, the paratungstate is in the form of large crystals.

The same product can also be obtained by slow partial neutralization of the $(NH_4)_2WO_4$ liquor by hydrochloric acid to pH = 6.5 and subsequent crystallization over a period of 7-12 hours. Repeated crystallization of the mother liquor yields additional quantity of crystals, after which the remaining tungsten is settled out as $CaWO_4$ and recycled.

Production of Tungsten Trioxide

Ammonium paratungstate decomposes at 250°C, and the tungstic acid, at 750-850°C. These products are calcined in small rotary kilns built of a stainless steel pipe and heated by electric power. Outgoing gases, containing chiefly water vapours, are dedusted in a sleeve filter.

Size of particles of resultant tungsten trioxide depends on temperature, which is also of a prime importance in subsequent processing stages of tungsten powder manufacture. Size of WO_3 particles is checked through bulk mass value or aggregate surface area, which is determined by adsorption of methanol vapours in a special installation.

67. Manufacture of Metallic Tungsten

Metallic tungsten may be manufactured either as a powder or a compact metal. Powder tungsten is obtained by reduction of tungsten trioxide by hydrogen or carbon.

Reduction by Hydrogen

Reduction may be divided into three steps

$$\left.\begin{aligned} 2WO_3 + H_2 &\rightarrow W_2O_5 + H_2O \\ W_2O_5 + H_2 &\rightarrow 2WO_2 + H_2O \\ WO_2 + 2H_2 &\rightarrow W + 2H_2O \end{aligned}\right\} K_p = \frac{P_{H_2O}}{P_{H_2}} \qquad (244)$$

Each subsequent step requires a higher temperature and a greater content of hydrogen in the gas mixture than the preceding one.

Industrially, tungsten trioxide is reduced in tube furnaces (Fig. 121). The steel pipe of such a furnace is heated electrically or by natural gas over a length of about 2 m, pipe

diameter being 50-100 mm. Tungsten trioxide is placed inside nickel boats which are gradually moved in an opposite direction to flow of hydrogen. Boats successively pass zones of ever greater temperatures and of drier hydrogen, then cool gradually, final cooling taking place inside a cooler located before the discharge end of the pipe. Peak temperature in the hottest furnace zone may attain 860°C.

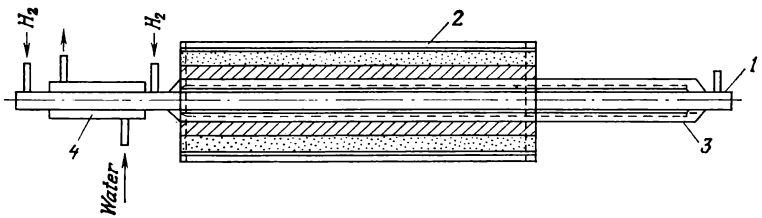

Fig. 121. Tube furnace for hydrogen reduction of tungsten trioxide
1—pipe; *2*—furnace shell; *3*—nichrome winding; *4*—cooler

Pure hydrogen for the reduction is obtained by electrolysis of water in reduction cells with iron or nickel electrodes partitioned by a membrane. The electrolyte is an alkali solution.

Hydrogen evolves at the cathode according to reaction

$$2H_2O + 2\bar{e} \rightleftarrows H_2 + 2OH^-; \quad E^\circ = -0\,83 \text{ V} \qquad (245)$$

while oxygen is given off at the anode in accordance with the reaction (25).

Before hydrogen is admitted into the furnace, it is cleaned of oxygen by passage through an incandescent copper wire cloth, platinum-coated asbestos or titanium sponge. Next, hydrogen is dried, its moisture being absorbed by soda lime, calcium chloride or silica gel. Remaining moisture is captured by phosphoric anhydride. Hydrogen that comes out of the furnace is cleaned of water vapours and re-used for reduction. Capacity of reduction furnaces is governed by the capacity of boats and their speed of motion. The faster the motion, the coarser are the powders.

Reduction is carried out in two steps, first, at 720°C to WO_2, the dioxide then being mixed with a fresh portion of tungsten trioxide and the treatment repeated at 860°C.

Multi-pipe furnaces, e.g., eleven-pipe ones, are more pro-

ductive. All the pipes are arranged in parallel in a single chamber heated by nichrome spiral heaters.

At larger plants, tungsten trioxide is reduced in rotary kilns built of a stainless steel pipe up to 4 m long and about 400 mm in diameter (Fig. 122). The pipe, heated from outside by an electric heater, is partitioned inside by perforated disks interconnected by ribs of steel angle bars. This arrangement prevents the material from moving at too fast a rate along the pipe and thus promotes better contact between the material and the flow of hydrogen.

Reduction by Carbon

The use of this simpler and cheaper method for manufacturing powder tungsten is possible whenever carbide impurities cause no objection on the part of consumers. The reducer then is gas black and other ash-free carbon materials.

Industrially, this process is carried out at 1400-1800°C either in electric tube furnaces with tubes of graphite or carbon (the tube being the heating resistor as well) or in graphite crucibles. The process yields a fine powder tungsten suitable for the production of hard carbide alloys.

Tungsten can also be obtained by direct reduction of tungstates in by-pass of the tungsten trioxide stage, as,

$$\left.\begin{aligned} CaWO_4 + 3C &\rightarrow CaO + W + 3CO \\ Na_2WO_4 + 3C &\rightarrow Na_2O + W + 3CO \end{aligned}\right\} \qquad (246)$$

Sodium salts are removed from the reduction products by washing in water, and calcium oxide, by dressing in gravity concentration tables. Resultant powders are suitable only for the alloying of steels or the manufacture of commercial tungsten alloys.

Manufacture of Ductile Tungsten

Ductile tungsten is obtainable as wire or sheets from a powder reduced by hydrogen only and containing not more than 0.05% of impurities. Size of powder particles should range from 0.5 to 6 micrometres and measure 2 to 3 micrometres across on the average.

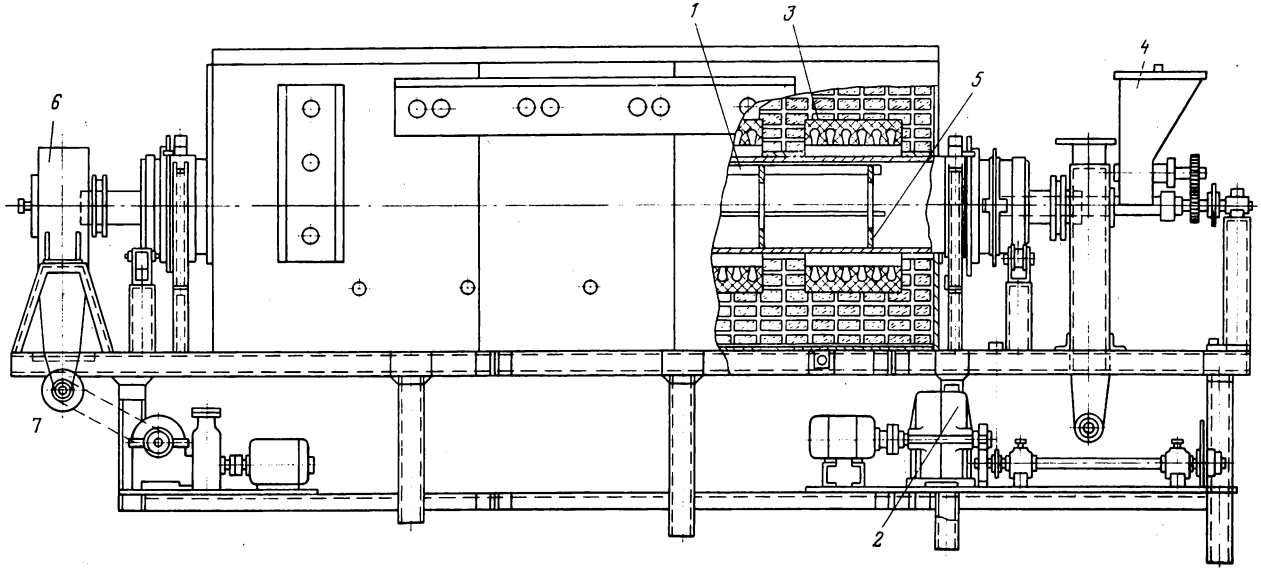

Fig. 122. Rotary kiln for hydrogen reduction of tungsten trioxide

1—steel pipe; *2*—kiln rotation drive; *3*—furnace shell and electric heater; *4*—charging hopper with feeder; *5*—steel perforated disks interconnected by angle bars; *6*—discharge device and hydrogen inlet; *7*—discharge mechanism

The powder is pressed at a force of 196-294 MN/m² (2.0-3.0 t/cm²) to bars which are regular rectangular prisms

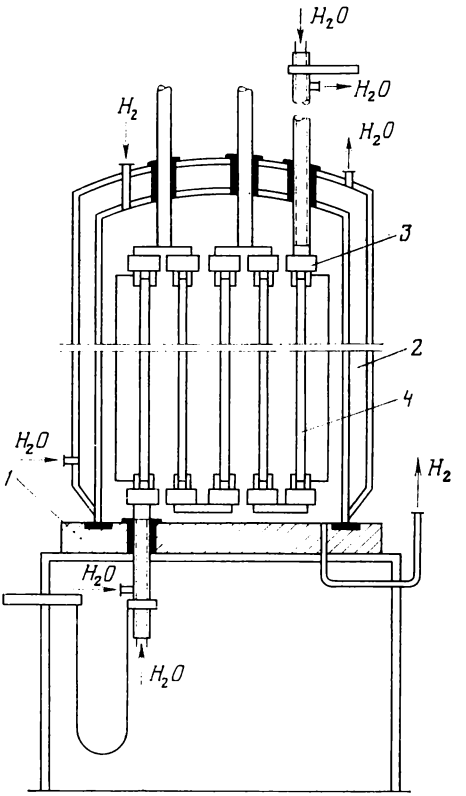

Fig. 123. Apparatus for sintering tungsten bars
1—steel slab; *2*—water-cooled hood; *3*—water-cooled contacts; *4*—series connected tungsten bars

with bases measuring 10 mm, and length, 600 mm. In pressing, powder particles are caused to move with respect to each other and thus to pack closely inside the mould. The resultant increase in area of mutual contact ensures mechanical strength of the blank. Friction between powder and walls of the mould is minimized by wetting the powder prior to pressing in a mixture of alcohol and glycerine or

of wax and gasoline. Bar strength is further enhanced by heating in hydrogen at 1150-1300°C, this removing the lubricating mixture, reducing films that separate particles and somewhat coarsening finer particles of tungsten.

Bars are placed inside boats upon a bed of tungsten powder or special liners of tungsten or molybdenum. Boats are heated in electric muffle furnaces in a stream of hydrogen and are gradually moved upstream with respect to hydrogen flow and to zones of ever increasing temperatures. Presintered bars are still mechanically weak, and to remedy to the defect, they are heated by passing electric current to a temperature close to melting point of tungsten, i.e., to 3000-3100°C. Bars are clamped between two water-cooled copper contacts of the sintering apparatus (Fig. 123), and a current is passed through them. This apparatus is assembled on a steel plate and isolated from the atmosphere by a bell with double water-cooled walls, the space underneath the bell being filled with hydrogen.

Sintering conditions are adjusted by a trial and error method. Determined first is a current that is required to cause melting of a test bar. Next, heating of bars is controlled on the indications of an ammeter, current intensity being gradually raised to 80 to 90% of the remelting current.

Overall duration of sintering is from 15 min to 1 hour. In the course of sintering, remaining impurities volatilize at high temperatures, bar density increases to 17-18.5 gram/cm^3, and porosity comes down to 10-15%.

Sintered bars can be swaged at 1300-1400°C in a hydrogen atmosphere, since they are sufficiently ductile. Special swaging machines first produce rods 2-3 mm in diameter, which are then hot drawn in several steps to yield wire down to 0.01 mm across.

Sheet tungsten is obtained by hot rolling in a hydrogen atmosphere of bars or similar blanks after the initial swaging.

Review Questions

1. Name the range of customary WO_3 contents in wolframite concentrates.

20-40; 40-60; 60-80.

2. What impurities are removed from Na_2WO_4 liquors before tungstic acid is precipitated?

Cu, Fe, SiO_2, P, As, Mo, Ca.

CHAPTER 12

METALLURGY OF MOLYBDENUM

68. Chemical Properties of Molybdenum

Molybdenum resembles tungsten in appearance and in chemical properties. The outer shell of molybdenum atom carries one electron and because of this molybdenum, as a metal, is more active than tungsten, although the difference is slight; molybdenum is also a metalloid of a maximum positive valency of 6.

Natural molybdenum of an atomic mass of 95.94 consists of seven stable isotopes: Mo^{92}, Mo^{94}, Mo^{95}, Mo^{96}, Mo^{97}, Mo^{98}, Mo^{100}. Molybdenum was separated for the first time ever by P. I. Hjelm in 1782, but has found industrial application at the beginning of this century only.

Melting and boiling point of molybdenum are lower than those of tungsten, but it should be considered a practically non-volatile element.

In the air, molybdenum begins to oxidize appreciably at a temperature of about 400°C. Above 600°C, oxygen of the air and water vapours oxidize molybdenum to MoO_3 fairly rapidly. With carbon and carbon monoxide, molybdenum forms at 1100°C a carbide Mo_2C, and with nitrogen at temperature above 1500°C, a nitride, probably Mo_2N.

With hydrochloric and sulphuric acids, molybdenum begins to react appreciably at 80-100°C only, while nitric acid and aqua regia dissolve it at low temperatures, as well, but fairly rapidly at over 100°C only.

In cold alkali liquors, molybdenum is stable, while hot alkalis tend to dissolve it gradually.

Higher oxide, molybdenum trioxide, MoO_3 is most stable. It melts at 795°C and boils at 1155°C. MoO_3 reacts with water to give a molybdic acid H_2MoO_4, known as fine crystals poorly soluble in water, and other isopolyacids (232) of a complex composition, or aquapolyacids. In alkali

liquors, molybdenum is present as ion MoO_4^{2-}, this corresponding to a series of salts, termed molybdates. Dioxide MoO_2 is less stable than the trioxide (MoO_3).

Affinity of molybdenum for sulphur is fairly great and is commensurate with that for oxygen, and this is why natural disulphide MoS_2 is of a frequent occurrence. A higher sulphide MoS_3 (233) is obtainable by synthesis.

Molybdenum compounds are used industrially for a number of purposes: MoS_2 serves as a lubricant, sodium molybdate Na_2MoO_4 is used in paint and varnish manufacture, oxides MoO_3 and MoO_2 are catalysts in organic substance manufacturing processes.

69. Raw Materials for Molybdenum Manufacture

Among the known molybdenum minerals, of chief commercial importance is molybdenite MoS_2. Some 99% of molybdenum are obtained from molybdenite ores, inclusive of copper-molybdenum ones.

Some ores also carry other molybdenum minerals, as, powellite $CaMoO_4$, molybdite $xFe_2O_3 \cdot yMoO_3 \cdot nH_2O$ and wulfenite $PbMoO_4$.

Molybdenum often associates in ores with tin, tungsten, arsenic, copper and bismuth; in copper molybdenum ores, molybdenum is an associate of copper.

Barren rock of molybdenum ores is represented chiefly by quartz, sericite and fluorite. Molybdenum ores, either occurring as nests and veins in quartzites or forming shots, generally carry 0.1-0.2% Mo, whereas copper-molybdenum ones, 0.03-0.05% Mo and up to 2% of copper.

Molybdenite can readily be flotated even by the addition of a frother only (pine oil). Practically, collectors introduced into the pulp are hydrocarbons, such as kerosene or oils. Intergrowths of MoS_2 and quartz are destroyed by stage grindings during cleanings of primary concentrate.

Copper-molybdenum ores are flotated, similarly to usual copper ores, to bulk concentrates, which are then separated to individual concentrates. Prior to a selective flotation, copper and other minerals are treated by sodium sulphide to remove the collector, and hydrocarbons are then added to float the molybdenite.

Recovery of molybdenum to concentrate from molybdenum ores approximates 90%, and from copper-molybdenum ores, 50-70%.

Customary range of composition of molybdenum concentrates is as follows, %: Mo, 47-50; P, 0.07-0.15; As, 0.07; Cu, 0.5-2.0; SiO_2, 5-7. Molybdenite often carries an isomorphic mixture of rhenium compounds, rhenium content being mere 0.0004-0.02%, but notwithstanding this low content molybdenum ores are the chief raw materials for the recovery of this disseminated metal.

70. Molybdenum Manufacturing Techniques

Molybdenum concentrates are first processed to pure molybdenum trioxide MoO_3, which is then reduced to metal either by hydrogen or carbon. Molybdenum powder is used for the manufacture of alloys or processed into a solid ductile metal by metalloceramic techniques, similarly to tungsten.

There are two chief flowsheets of molybdenum trioxide production. One of these is based on the ready volatility of MoO_3, and direct volatilization of molybdenum trioxide from a roasted concentrate. The other flowsheet involves the leaching of MoO_3 of the roasted concentrate by ammonia water with the formation of $(NH_4)_2MoO_4$ liquors.

Impurities are removed from these liquors, and molybdic acid is precipitated according to reaction

$$(NH_4)_2MoO_4 + 2HCl \rightarrow \downarrow H_2MoO_4 + 2NH_4Cl \qquad (247)$$

or crystallized from the same liquor after ammonia content has been brought down by vaporization of ammonium paramolybdate $(NH_4)_6Mo_7O_{24}$.

Remaining molybdenum is settled out of the final mother liquor as calcium molybdate or iron molybdate, which are both processed by a separate technique.

Molybdenum trioxide is obtained from molybdic acid or from ammonium paramolybdate by calcining these substances at 400-450°C in muffle or other types of furnaces.

A flowsheet for processing molybdenum concentrates by an ammonia technique is shown in Fig. 124.

In an alternative technique, molybdenum trioxide is volatilized from a roasted concentrate at 900-1100°C, its

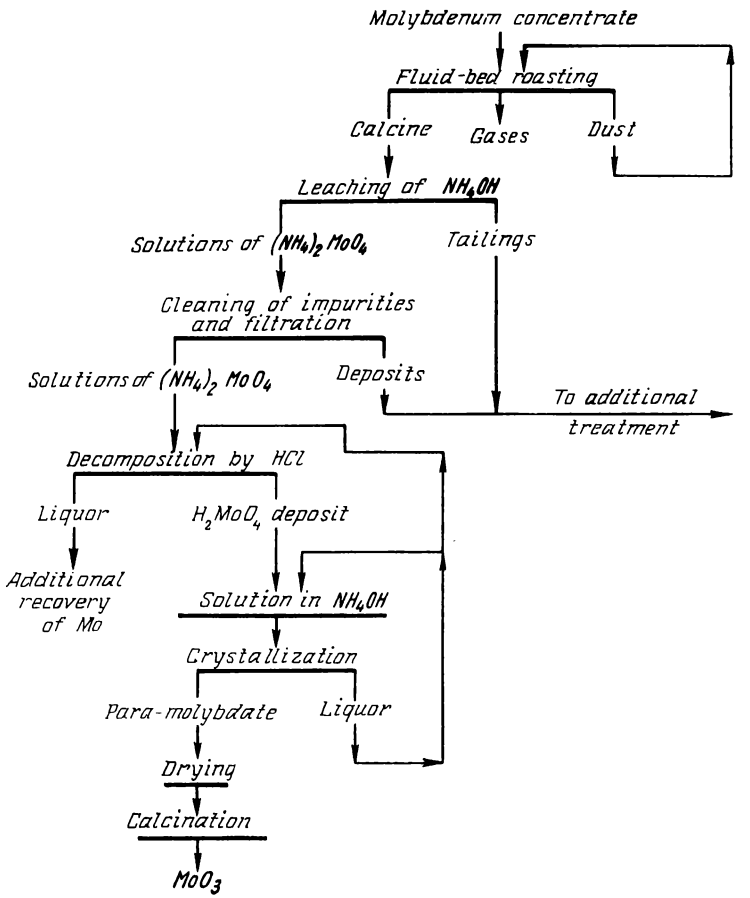

Fig. 124. Treatment of molybdenum concentrates by ammonia technique

volatilization being speeded up by removal of vapours in a stream of air. Volatilized products are settled out in dust collectors.

The yield of molybdenum trioxide from concentrates containing large amounts of calcium, iron and copper is rather low, as these elements tend to form stable molybdates even in roasting. Lead molybdate is volatile, and it contaminates the volatilized product, if the concentrate carries lead.

Volatilization is simpler than the ammonia technique, but it is advantageous in application to very rich and pure concentrates only.

Ammonia leaching or volatilization often allow a recovery of mere 80% of molybdenum from its concentrate, and, therefore, waste products, which still carry up to 20% of the starting amount of molybdenum, require additional processing.

Low-grade molybdenum concentrates, ore dressing middlings and ammonia leaching and volatilization wastes are leached by NaOH or fused together with soda at 650-700°C, then leached by water. Next, calcium or iron molybdate, directly suitable for smelting to ferromolybdenum, is settled out of the resultant liquors which contain molybdenum as Na_2MoO_4.

71. Manufacture of Molybdenum by Ammonia Technique

Roasting of Molybdenum Concentrates

The chief reaction in roasting is the oxidation of molybdenite

$$2MoS_2 + 7O_2 = 2MoO_3 + 4SO_2;$$

$$\Delta H_{298^\circ} = -1956 \text{ kj (468 kcal)} \qquad (248)$$

Sulphides of copper, iron and other metals oxidize according to similar reactions to give respective oxides and sulphurous gas.

To avoid loss of highly volatile MoO_3, roasting temperature should be kept below 650°C, so as to prevent its melting from local overheating. Given below are saturated vapour pressures of molybdenum trioxide:

Temperature, °C	650	800	900
p, N/m^2 (mm Hg)	6.7 (0.05)	1334 (10.1)	7185 (53.9)
Temperature, °C	1000	1100	1150
p, N/m^2 (mm Hg)	26 433 (198.3)	81 903 (476.2)	101 308 (760.0)

Resultant calcine carries, because of a relatively low roasting temperature, a considerable amount of sulphur combined in sulphates of iron, copper, zinc, lead and calcium.

Molybdenum trioxide, being an acid oxide, reacts in roasting with oxides of copper, iron, lead and calcium to give molybdates, e.g., $CuMoO_4$, $FeMoO_4$, $CaMoO_4$, $PbMoO_4$ and others.

Roasting was formerly conducted in multi-hearth mechanical roasters.

In recent years, molybdenum concentrates have been successfully treated in fluid-bed roasters. Besides a sharp increase in productivity, this has improved the quality of the calcine, as the formation of molybdates has been greatly reduced because of lesser contact between MoO_3 and oxides. Ammonia leaching of fluid-bed roaster calcine allows a recovery to liquors of up to 92% Mo as compared to 80% recovery from multi-hearth roaster calcine.

Rhenium concentrates in dusts collected in electrostatic precipitators as its heptoxide Re_2O_7 is volatile.

Leaching MoO_3 *by Ammonia Water*

Extraction of molybdenum by ammonia liquors is based on the reaction

$$MoO_3 + 2NH_4OH \rightarrow (NH_4)_2MoO_4 + H_2O \qquad (249)$$

Liquors are contaminated by copper and zinc, whose sulphates and oxides form water-soluble ammonia complexes through partial solution of divalent iron

$$Fe(OH)_2 + 2NH_4^+ \rightleftarrows Fe^{2+} + 2NH_4OH \qquad (250)$$

$$K_{239} = \frac{a^2_{NH_4OH} \cdot a_{Fe^{2+}}}{a^2_{NH_4^+}} = \frac{Sp_{Fe(OH)_2}}{K^2_{NH_4OH}}$$

$$pK_{239} = pSp_{Fe(OH)_2} - 2pK_{NH_4OH} = 15 - 2 \cdot 4.75 = 5.5$$

Assuming $a_{NH_4OH} = a_{NH_4^+} = 1$, we obtain $\log a_{Fe^{2+}} = -5.5$,

$$[Fe^{2+}] \approx a_{Fe^{2+}} \simeq 1.8 \cdot 10^{-4} \text{ gram/litre}$$

If $a_{NH_4^+}$ is retained unchanged, and excess of NH_4OH assumed equal to $a_{NH_4OH} = 0.01$ mole/litre, the result will be

$$[Fe^{2+}] \approx 1.8 \text{ gram/litre}$$

Silica and other components of the barren rock remain in the insoluble residue. A pre-washing of roasted concentrate by water reduces the contamination of liquors from leaching.

Leaching is carried out in steel drum-type gas-tight horizontal apparatus or in tanks fitted with stirrers. Roasted concentrate is treated twice by a fresh 10% ammonia liquor. Sometimes second leaching is preceded by roasting of tailings of the first leaching. After a second leaching, residues contain up to 10% Mo which is extracted by alkali or soda techniques in a separate process. Incomplete recovery of molybdenum to ammonia liquors is due to formation of molybdates in roasting or incomplete oxidation of MoS_2. The content of MoO_3 in ammonia liquors attains 140-190 gram/litre.

Ammonia liquors should be purified to remove copper and remaining iron. $Fe(OH)_2$ is partly soluble as per (250) and forms colloid liquors. Both these contaminants are settled out as sulphides by ammonia sulphide.

$$Cu(NH_3)_4^{2+} + S^{2-} + 4H_2O \rightarrow \downarrow CuS + 4NH_4OH \qquad (251)$$

$$Fe(OH)_2 + (NH_4)_2S \rightarrow \downarrow FeS + 2NH_4OH \qquad (252)$$

Excess ammonium sulphide and molybdate give thiosalts, the liquor thus being contaminated by sulphur.

Lead nitrate is added to the liquor to decompose MoS_4^{2-}

$$(NH_4)_2MoS_4 + 4Pb(NO_3)_2 + 8NH_4OH \rightarrow$$

$$\rightarrow \downarrow 4PbS + (NH_4)_2MoO_4 + 4H_2O + 8NH_4NO_3 \qquad (253)$$

A minimum excess of lead nitrate should be used as it binds molybdenum in an insoluble lead molybdate.

Sulphide residues are filtered, while molybdic acid or ammonium paramolybdate is extracted from the purified liquor.

Precipitation of Molybdic Acid or Ammonium Paramolybdate

Precipitation of molybdic acid according to reaction

$$(NH_4)_2MoO_4 + 2HCl \rightarrow H_2MoO_4 + 2NH_4Cl \qquad (254)$$

by pouring a liquor of ammonium molybdate to hydrochloric acid gives fine crystalline poorly filtrable and washable deposits. A gradual addition of the acid to the $(NH_4)_2MoO_4$ liquor until pH attains 3.5-4 results in improved filtrability of the deposit because of a formation of polymolybdates of variable composition. After some 95% of molybdenum is settled out, the remaining portion is extracted as H_2MoO_4 by a further addition of HCl to obtain a pH of 2-2.5. Molybdic acid is a recycled semi-product.

Solubility of molybdic acid in water is 1.55 gram/litre at 20°C, and, therefore, the precipitation is incomplete. Remaining molybdenum is settled out from the filtrate by calcium chloride as calcium molybdate $CaMoO_4$.

High-purity molybdic acid is obtained by dissolving polymolybdate deposit in ammonia and repeating the precipitation. Content of impurities in a twice precipitated acid is about 0.1%.

A frequent practice is to extract molybdenum from ammonium liquors as ammonium paramolybdate.

Solution of polymolybdate in ammonium water yields liquors of densities from 1.41 to 1.43 gram/cm^3. When cooled in crystallizers, the solutions give off coarse crystals of ammonium paramolybdate. Mother liquor is returned to solution and partly to decomposition by HCl, build-up of impurities thus being avoided.

Production of Molybdenum Trioxide

Calcining molybdic acids of ammonium paramolybdate in muffle or other types of furnaces at 400-450°C yields molybdenum trioxide.

Similarly to paramolybdate, molybdenum trioxide is suitable for the manufacture of ferroalloys, but it is more often employed for the production of molybdenum powder and ductile molybdenum.

Manufacture of Molybdenum Powder and Ductile Molybdenum

Molybdenum trioxide is reduced to metal in three steps corresponding to three molybdenum oxides

$$\left.\begin{aligned} 2MoO_3 + H_2 &= Mo_2O_5 + H_2O \\ Mo_2O_5 + H_2 &= 2MoO_2 + H_2O \\ MoO_2 + 2H_2 &= Mo + 2H_2O \end{aligned}\right\} K_p = \frac{P_{H_2O}}{P_{H_2}} \qquad (255)$$

The first reaction proceeds more readily than that in the manufacture of tungsten, while the last one, by contrast, calls for higher temperatures and a lesser content of water vapours in gases. Partly reduced MoO_3 melts at 500-600°C, and to avoid this, the first reduction step is carried out at 450°C, and the second, at 1100°C.

Molybdenum powder is pressed at 2.9 MN/m² (3000 kgf/cm²) into bars which are then processed similarly to tungsten bars. Presintering is conducted at a temperature of about 1200°C, and final sintering, at 2200-2400°C. Sintered bars are swaged and drawn at temperatures by 100-300°C lower than those for tungsten.

Whenever large ingots and blanks are required, molybdenum is remelted in vacuum arc furnaces. The arc is struck between a consumable electrode from sintered molybdenum powder and molten metal in a water-cooled copper mould, similar to that used in melting titanium.

Introduced in recent years was an electron-beam melting of molybdenum which allows a removal of many volatile impurities by a prolonged holding of molten metal in a deep vacuum.

The principle of electron-beam melting can readily be understood from a schematic diagram in Fig. 125. A beam of electrons is emitted by a hot cathode from tungsten and tantalum which is at a highly negative potential. Penetra-

ting through a hole of earthed anode *2*, the beam is focussed by an electromagnetic coil *4* similarly to focussing of light by lenses, and is directed against the end of the blank from pressed bars. A high kinetic energy of electrons as they impinge upon the blank is turned to heat which thus melts the blank.

The system for accelerating and focussing the electron beam, the electron gun, operates in a deep vacuum, of the

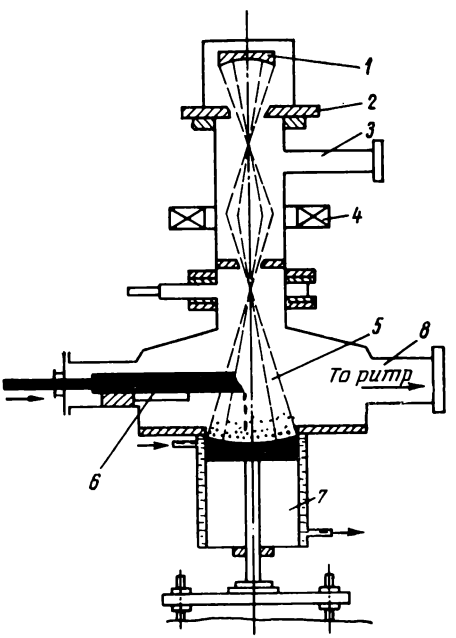

Fig. 125. Apparatus for electron beam melting of molybdenum
1—cathode of electron gun; *2*—anode of electron gun; *3*—pipe for sucking air out of gun; *4*—solenoid; *5*—beam of electrons; *6*—blank for re-melting; *7*—water-cooled copper mould; *8*—pipe for sucking air out of melting chamber

order of $133.3 \cdot 10^{-4}$ to $133.4 \cdot 10^{-5}$ N/m^2 (10^{-4} to 10^{-5} mm Hg). Energy is utilized best by providing a voltage of 30-35 kV when the fraction of the side X-ray emission is at its least, while the system's efficiency attains 95%,

Large molybdenum ingots can be obtained by gradually lowering the mould bottom.

Electron-beam melting is also used to produce ingots of other refractory metals.

Review Questions

1. Name customary content of molybdenum in ores.
0.01%; 0.1%; 1%; 10%.
2. What heavy nonferrous metal is often associated with molybdenum in ores?
Cu, Pb, Zn, Ni.
3. What impurities lower recovery of molybdenum from roasted concentrates by NH_4OH liquors?
P, As, SiO_2, Pb, Cu, Fe, Ca.

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USSR, 129820, Moscow, I-110, GSP, Pervy Rizhsky Pereulok, 2,
MIR Publishers.

Printed in the Union of Soviet Socialist Republics